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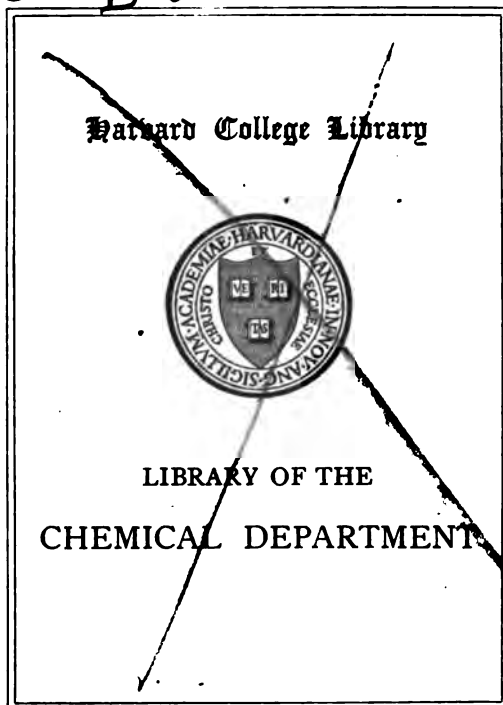
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THE METALLOGRAPHY AND HEAT TREATMENT OF IRON AND STEEL

BY

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Massachusetts Institute of Technology*

*SECOND EDITION (SEVENTH THOUSAND)
WITH REVISED CHAPTER I*

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TO
THE MEMORY OF
My Father
I REVERENTLY AND LOVINGLY
DEDICATE THIS BOOK

PREFACE TO THE SECOND EDITION

THE sale in less than three years of two impressions of the first edition of this book justifies the author's belief expressed at the time that there was a need in the educational and industrial world of a treatise on the metallography of iron and steel such as he has endeavored to supply. Dealing with a science so young, and therefore still in full growth, it was to be expected that even after so short a period as three years there would be need of a revised edition that recent progress might be put on record and a more faithful picture offered of its present status. The necessary revisions and additions have been made to the best of the author's ability. Nearly every chapter has been revised, while some fifty pages of new text have been added and nearly one hundred new illustrations used. With the exception of the last sixty-four pages, the book has been entirely reset. In view of the fact that so large a portion of this work is devoted to the study of the heat treatment of iron and steel, the new title, namely, "The Metallography and Heat Treatment of Iron and Steel," appears to be more accurately descriptive of its contents.

In the present edition, the author has continued to follow the course previously adopted by him, to utilize the best illustrations available rather than to use his own to the exclusion of others. Too many books purporting to be treatises on certain subjects are merely expositions of the author's views to the belittling of the opinions and work of others. Authors of treatises should be just and impartial and should not give undue prominence to their own views and opinions. This, obviously, they owe to their readers and to the public in general. The author of this book hopes that he has succeeded in adhering faithfully to that belief and, if he has failed in ever so small a degree, it has been unintentional.

Of the 338 illustrations reproduced exclusive of illustrations of apparatus, 80 were prepared by the author himself, 82 by others in his laboratory, and 25 by correspondence course students. The author records here his indebtedness to the following gentlemen for illustrations borrowed from them, the figures in parentheses indicating the number in each case: Messrs. Andrews (2), Arnold (5), Bayley (1), Belaiew (5), Benedicks (2), Brearley (2), Carpenter and Keeling (2), Chappell (1), Coe (1), Sherard Cowper-Coles (1), Desch (7), Edwards (1), Ewing and Rosenhain (2), Franklin (4), Gørens (8), Guillet (16), Gulliver (3), Houghton (1), Law (7), Levy (1), Longmuir (2), Maurer (1), Mellor (1), Osmond (20), Peirce (4), Pulsifer (1), Roberts-Austen (3), Robin (1), Roland-Gosselin (1), Rosenhain (7), Rooze-

boom (1), Ruff (1), Saladin (2), Sorby (1), Stead (19), Tschermak (3), Tschernoff (1), Upton (1), Wittorff (1), Wüst (3), Ziegler (1).

He also takes this opportunity of expressing his appreciation of the many kind and helpful criticisms and suggestions received from fellow-workers and other correspondents.

The method which the author has always followed in his teaching of metallography to postpone until the closing chapters the study of the equilibrium diagram and of the phase rule rather than to introduce the subject with these complex, and, therefore, at the time, forbidding, considerations has been adversely criticized by a few, but on the whole he believes that it has won out and he is more convinced than ever that it is the most effective and otherwise satisfactory method to follow.

ALBERT SAUVEUR.

HARVARD UNIVERSITY,
Cambridge, Massachusetts,
November 17, 1915.

The time has arrived for a new imprint of this book, but the author is abroad and cannot undertake a thorough revision in the near future.

The publishers therefore content themselves with the correction of minor typographical errors, except in Chapter I where recent rapid developments in photomicrographic apparatus have made it advisable to replace the illustrations of obsolete apparatus with those of improved types. This affects most of the illustrations from Figure 11 to Figure 37 inclusive.

SAUVEUR AND BOYLSTON.

CAMBRIDGE, MASSACHUSETTS,
July 18, 1918.

PREFACE TO THE FIRST EDITION

WHILE several excellent books on metallography have been published and while numerous papers on the metallography of iron and steel have appeared in the scientific and technical press, a well-balanced, specific, and comprehensive treatise on the subject has not heretofore been written. In the belief that there is a real and urgent need of such a treatise the author has endeavored to supply it, craving for his effort the indulgent criticism of his readers. He offers his book to those seeking self-instruction in the metallography of iron and steel, their special needs having been carefully considered in the arrangement of the lessons; he offers it to teachers and students trusting that they will find it valuable and suggestive as a text-book; he offers it to manufacturers and users of iron and steel in the belief that he has given due weight to the practical side of the subject and has avoided discussions of ill-founded or purely speculative theories; he offers it to the general reader interested in the scientific or practical features of the metallography of iron and steel, as the language used should be readily understood by those lacking specialized knowledge of the subject; he offers it to experts in the hope that they will find it not entirely devoid of original thought, original treatment, and suggestiveness.

In the matter of illustrations and especially of photomicrographs the author's aim has been to utilize the best available, using his own or those taken in his laboratory only when no better ones have, to his knowledge, been published by others. The original source of every illustration has been indicated and the author desires to express his indebtedness to the following writers, the figures in parenthesis showing the number of illustrations from each: Andrews (3), Arnold (7), Bayley (1), Belaiew (5), Brearley (2), Carpenter and Keeling (1), Sherard Cowper-Coles (1), Desch (4), Edwards (2), Ewing and Rosenhain (2), Guillet (18), Gœrens (9), Gulliver (2), Hall (1), Houghton (1), Kroll (1), Law (8), Levy (1), Longmuir (2), Matwieff (1), Maurer (1), Mellor (1), Osmond (17), Roberts-Austen (1), Robin (1), Roland-Gosselin (1), Rosenhain (2), Saladin (2), Sorby (1), Stead (13), Tschermak (3), Tschernoff (1), Wüst (5), Ziegler (1). All illustrations not otherwise inscribed are the author's.

The author cannot refrain from expressing here the sorrow and sense of personal loss he experienced when the news was received, while this book was passing through the press, of the death of Floris Osmond, for to the author, as no doubt to many others, Osmond's work and Osmond's life have been an inspiration. Osmond belonged to that admirable class of French scientists, who, like Pasteur and Berthelot, have so lofty a conception of the duty of the scientist that they give to the world the fruit of

their genius and of their untiring labors with no thought of monetary return or even of honorary recognition. If Sorby was the pioneer of metallography and Tschernoff its father, Osmond has been its torch-bearer for he, more than any other, has been our guide. While he is no longer with us, his light will long continue to burn and to show the way to promising and productive fields of research.

The author desires to place on record his warm appreciation of the assistance he received from Mr. H. M. Boylston in passing this book through the press, and also for many valuable suggestions.

ALBERT SAUVEUR.

HARVARD UNIVERSITY,
CAMBRIDGE, MASSACHUSETTS,
August 19, 1912.

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INTRODUCTION

THE INDUSTRIAL IMPORTANCE OF METALLOGRAPHY ¹

Twenty years ago the science of metallography was practically unknown and it is only within the last fifteen years that it has been seriously considered by metal manufacturers and consumers as a valuable method of testing and investigating. That so much has been accomplished in so short a time is highly gratifying to the many workers, practical or scientific, who have contributed by their efforts to the progress of metallography.

To realize the practical importance of metallography it should be borne in mind that the physical properties of metals and alloys — that is, those properties to which these substances owe their exceptional industrial importance — are much more closely related to their proximate than to their ultimate composition, and that microscopical examination reveals, in part at least, the proximate composition of metals and alloys, whereas chemical analysis seldom does more than reveal their ultimate composition.

The analytical chemist may tell us, for instance, that a steel which he has analyzed contains 0.50 per cent of carbon, without our being able to form any idea as to its properties, for such steel may have a tenacity of some 75,000 lbs. per square inch or of some 200,000 lbs., a ductility represented by an elongation of some 25 per cent, or practically no ductility at all; it may be so hard that it cannot be filed or so soft as to be easily machined, etc.

The metal microscopist, on the contrary, on examining the same steel will report its structural, i.e. its proximate, composition, informing us that it contains, for instance, approximately 50 per cent of ferrite and 50 per cent of pearlite, and we know at once that the steel is fairly soft, ductile, and tenacious; or he may report the presence of 100 per cent of martensite, and we know that the steel is extremely hard, very tenacious, and deprived of ductility.

Which of the two reports is of more immediate practical value, the chemist's or the metallographist's? Surely, that of the metallographist.

Nor is it only in the domain of metals that we find such close relationship between properties and proximate composition, for, on the contrary, it is quite true of all substances. How many organic bodies, for instance, have practically the same ultimate composition and still are totally unlike in properties because of their different proximate composition, i.e. different grouping and association of their ultimate constituents. If we were better acquainted with the proximate composition of substances many unexplained facts would become clear to us.

Unfortunately the chemist too often is able to give us positive information in regard to the proportion of the ultimate constituents only, his reference to proximate

¹ Abstracted from a paper presented at the Congress of Technology at the fiftieth anniversary of the granting of the charter of the Massachusetts Institute of Technology, April, 1911.

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analysis being of the nature of speculation. Ultimate analysis has reached a high degree of perfection in regard to accuracy as well as to speed of methods and analytical chemists have built up a marvelous structure calling for the greatest admiration, their searching methods never failing to lay bare the ultimate composition of substances. But how much darkness still surrounds the proximate composition of bodies and how great the reward awaiting the lifting of the veil!

The forceful and prophetic writing in 1890 of Prof. Henry M. Howe naturally comes to mind. Speaking of the properties and constitution of steel, Professor Howe wrote:

"If these views be correct, then, no matter how accurate and extended our knowledge of ultimate composition, and how vast the statistics on which our inferences are based, if we attempt to predict mechanical properties from them accurately we become metallurgical Wigginses . . .

"Ultimate analysis never will, proximate analysis may, but by methods which are not yet even guessed at, and in the face of fearful obstacles.

"How often do we look for the coming of the master mind which can decipher our undecipherable results and solve our insoluble equations, while if we will but rub our own dull eyes and glance from the petty details of our phenomena to their great outlines their meaning stands forth unmistakably; they tell us that we have followed false clues and paths which lead but to terminal morasses. In vain we flounder in the sloughs and quagmires at the foot of the rugged mountain of knowledge seeking a royal road to its summit. If we are to climb, it must be by the precipitous paths of proximate analysis, and the sooner we are armed and shod for the ascent, the sooner we devise weapons for this arduous task, the better.

"By what methods ultimate composition is to be determined is for the chemist rather than the metallurgist to discover. But, if we may take a leaf from lithology, if we can sufficiently comminute our metal (ay, there's the rub!) by observing differences in specific gravity (as in ore dressing), in rate of solubility under rigidly fixed conditions, in degree of attraction by the magnet, in cleavage, luster, and crystalline form under the microscope, in readiness of oxidation by mixtures of gases in rigidly fixed proportions, we may learn much.

"Will the game be worth the candle? Given the proximate composition, will not the mechanical properties of the metal be so greatly influenced by slight and undeterminable changes in the crystalline form, size, and arrangement of the component minerals, so dependent on trifling variations in manufacture as to be still only roughly deducible?"

The above was written before the days of metallography, or at least when metallography had barely appeared in the metallurgical sky and when no one yet had fancied what would be the brilliant career of the newcomer. Metallography has done much to supply the need so vividly and timely depicted by Professor Howe, precisely because by lifting a corner of the veil hiding from our view the proximate composition of metals and alloys it has thrown a flood of light upon the real constitution of these important products. Has the game been worth the candle? Will any one hesitate to answer in the affirmative Professor Howe's question?

Professor Howe with his usual acumen was conscious of the fact that proximate analysis, while likely to reveal a great deal more of the constitution of metals than ultimate analysis ever could, might still leave us in such ignorance of their physical structure as to throw but little additional light upon the subject. His fear was cer-

tainly well founded and surely if the proximate composition had been obtained by chemical analysis it would indeed have told us little of the structure or anatomy of the metals. In the domain of proximate composition chemistry cannot do more for the metallurgist than it does for the physician.

Invaluable information chemistry does give, without which both the physician and the metallurgist would be in utter darkness, but it throws little or no light upon the anatomy of living or inanimate matter. Its very methods which call for the destruction of the physical structure of matter show how incapable it is to render assistance in this, our great need.

The parallel drawn here between metals and living matter is not fantastic. It has been aptly made by Osmond, who said rightly that modern science was treating the industrial metal like a living organism and that we were led to study its anatomy, i.e. its physical and chemical constitution; its biology, i.e. the influence exerted upon its constitution by the various treatments, thermal and mechanical, to which the metal is lawfully subjected; and its pathology, i.e. the action of impurities and defective treatments upon its normal constitution.

Fortunately metallography does more than reveal the proximate composition of metals. It is a true dissecting method which lays bare their anatomy — that is, the physical grouping of the proximate constituents, their distribution, relative dimensions, etc., all of which necessarily affect the properties. For two pieces of steel, for instance, might have exactly the same proximate composition — that is, might contain, let us say, the same proportion of pearlite and ferrite and still differ quite a little as to strength, ductility, etc., and that because of a different structural arrangement of the two proximate constituents; in other words, because of unlike anatomy.

It is not to be supposed that the path trodden during the last score of years was at all times smooth and free from obstacles. Indeed, the truth of the proverb that there is no royal road to knowledge was constantly and forcibly impressed on the mind of those engaged in the arduous task of lifting metallography to a higher level.

Its short history resembles the history of the development of all sciences. At the outset a mist so thick surrounds the goal that only the most courageous and better equipped attempt to pierce it and perchance they may be rewarded by a gleam of light. This gives courage to others and the new recruits add strength to the besieging party. Then follow the well-known attacking methods of scientific tactics and strategy, and after many defeats and now and then a victorious battle the goal is in sight, but only in sight and never to be actually reached, for in our way stands the great universal mystery of nature: what is matter? what is life?

Nevertheless there is reward enough for the scientist in the feeling that he has approached the goal, that he has secured a better point of vantage from which to contemplate it. The game was worth the candle. And if scientific workers must necessarily fail in their efforts to arrive at the true definition of matter, whatever be the field of their labor, they at least learn a great deal concerning the *ways of matter*, and it is with the ways of matter that the material world is chiefly concerned. Hence the usefulness of scientific investigation, hence the usefulness of metallography.

Like any other science with any claim to commercial recognition, metallography has had first to withstand the attack and later to overcome the ill-will and reluctance of the so-called "practical man" with a decided contempt for anything scientific. He represents the industrial philistine clumsily standing in the way of scientific applications to industrial operations. Fortunately, while his interference may retard

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progress, it cannot prevent it. Had he had his own way neither the testing machine, nor the chemical laboratory, nor the metallographical laboratory, nor the pyrometer would ever have been introduced in iron and steel works.

Speaking in 1904 of the practical value of metallography in iron and steel making, the author wrote the following, which it may not be out of place to reproduce here: "History, however, must repeat itself, and the evolution of the metallographist bids fair to be an exact duplicate of the evolution of the iron chemist; the same landmarks indicate his course; distrust, reluctant acceptance, unreasonable and foolish expectation from his work, disappointment because these expectations were not fulfilled and finally the finding of his proper sphere and recognition of his worth. The metallographist has passed through the first three stages of this evolution, is emerging from the fourth, and entering into the last. For so young a candidate to recognition in iron and steel making this record is on the whole very creditable."

We may say to-day that he has definitely entered the last stage and that the adverse criticisms still heard from time to time, generally from the pen or mouth of ignorant persons, are like the desultory firing of a defeated and retreating enemy.

In the United States alone the microscope is in daily use for the examination of metals and alloys in more than two hundred laboratories of large industrial firms,¹ while metallography is taught in practically every scientific or technical school.

A. S.

HARVARD UNIVERSITY,
February, 1912.

¹ As the second edition of this book goes to press, it may be safely affirmed that not less than four hundred industrial laboratories in the United States are equipped for metallographical testing.

In July, 1918, there is good evidence that not less than nine hundred metallurgical microscopes are in use in nearly as many industrial and scientific laboratories in the United States.

CHAPTER I

APPARATUS FOR THE METALLOGRAPHIC LABORATORY ¹

Those apparatus which the author has found most satisfactory are described in this chapter at some length; others more briefly in Chapter III.

THE MICROSCOPE

While any good microscope of the ordinary type, substantially built and provided with a satisfactory fine adjustment, may be used with a certain degree of success for the examination of metals and alloys, those who are restricted to its use will soon find themselves seriously handicapped in several directions and unable to obtain the desired results. The following considerations will make this clear.

The Stage. — Ordinary microscope stands being constructed for the examination of objects by transmitted light, i.e. by light proceeding from below the stage and passing through the object on its way to the eye, are provided with fixed stages. This, however, is a serious objection when the instrument is applied to the examination of metals and other opaque objects, which must necessarily be illuminated by light directed upon them from *above* the stage, and which therefore require the use of an "illuminator" attached to the objective and consequently moving with it. It will be readily understood that it is of considerable importance that the position of this illuminator, and therefore of the objective to which it is attached, be kept constant, once the necessary adjustments are effected, since any change in its position would require a readjustment of the source of light, the condensing lenses, diaphragm, etc. To that effect the stage should be provided with a rack and pinion motion by means of which the coarse focusing at least may be done (Fig. 1).

This rack and pinion motion of the stage, moreover, permits of a much greater working distance, allowing plenty of room for the insertion of the illuminator and nose-piece, the use of specimen holders, and the examination of bulky specimens with low-power objectives. In the microscope illustrated in Figure 1, the working distance measures over 5 inches as against 4 inches or less in ordinary stands.

By not departing more than necessary from the usual construction of microscopes, none of the essential features required for the examination of transparent preparations need be sacrificed, and the full efficiency of the microscope is retained for such examination, sub-stage condensers, polarizing prisms, etc., being readily attached when needed. The possibility of applying his instrument to all kinds of microscopical work with equally satisfactory results should appeal strongly to the metallographist, for there is no laboratory where, occasionally at least, examination of transparent objects is not desirable or even imperative.

¹ Abstracted in part from papers by the author on "Apparatus for the Microscopical Examination of Metals," American Society for Testing Materials, Vol. X, 1910.



Fig. 1. — Metallurgical microscope, eye-piece, vertical illuminator, objective, magnetic specimen holder, and mechanical stage. (0.5 actual size.)



Fig. 2. — Student microscope. (0.5 actual size.)

Less expensive but satisfactory microscopes are shown in Figures 2 and 3. The latter illustration includes an auxiliary tube inserted between the objective and illuminator for the examination of large samples which may be placed on the base of the microscope or supported in some other suitable way below the stage.

(a) *Plain Stages.* — While a mechanical stage adds greatly to the convenience of the manipulations, a plain stage may be used with satisfactory results. It should be provided with strong clips to hold in place the specimen holders soon to be described, and should preferably be circular and revolving (Fig. 4). When provided with centering screws like the stage of the stand illustrated in Figure 1, the object may be moved gently while under examination, a very desirable feature especially when using high-power objectives, in which case the moving of the object entirely by hand is very jerky. In order to derive the full benefit of the use of the magnetic holder described later, the central opening of the stage should not be less than $1\frac{1}{4}$ inches in diameter.

(b) *Mechanical Stages.* — The great superiority of a mechanical stage permitting, as it does, a systematic examination of the object over its entire surface, need not be insisted upon. In connection with the magnetic holder it makes it possible, moreover, to examine repeatedly and at any time the same spot of any specimen, as will soon be explained. The mechanical stage illustrated in Figure 5 has been especially designed to fit the metallurgical microscope (Fig. 1), and is very readily substituted for the plain stage. The central opening measures $1\frac{5}{8}$ inches in diameter, permitting the convenient use of the magnetic holder.

Objectives. — Ordinary achromatic objectives give satisfactory results. They should, however, be corrected for uncovered objects, as the placing of cover glasses over bright metallic surfaces is accompanied by light reflection causing loss of clearness and definition.

Some believe that the objectives should be provided with short mounts so as to bring the reflector of the vertical illuminator as near the back lens of the objective as possible, and thus, in their opinion, materially decreasing the amount of glare caused by the reflection of light by the lenses of the objectives. They are advisable only when a prism vertical illuminator or one with a backed mirror reflector is used. Three objectives, one of low, one of medium, and one of high power, will generally suffice for metallographic work. The following focal lengths are recommended: 32-mm. or $1\frac{1}{3}$ -in., 16-mm. or $\frac{2}{3}$ -in., and 4-mm. or $\frac{1}{6}$ -in. These objectives are shown in Figure 6. The 32-mm. objective is provided with a society screw at its lower end in order that the vertical illuminator may be inserted between the objective and the object, this being desirable with very low-power lenses. In case higher power is needed, a 1.9-mm. or $\frac{1}{12}$ -in. oil immersion objective will be found very satisfactory. When a very low-power lens is required, as for instance in the examination of fractures or of very coarse structures, a 48-mm. or 2-in. objective will give good results. It is suggested that it be provided at its lower end with a society screw to permit the attachment of the vertical illuminator, which in the case of such low-power lenses should be placed between the object and the objective, as explained later.

Eye-Pieces. — With achromatic objectives ordinary Huygenian eye-pieces are used. Two eye-pieces, respectively of 1-in. and 2-in. focal length, will generally cover the range of magnification needed.

For the taking of photomicrographs, projection eye-pieces are said to possess some superiority, especially when high-power objectives are used, as they then yield



Fig. 3. — Student microscope fitted with auxiliary tube.



Fig. 4. — Plain revolving stage, magnetic specimen holder, and specimen.



Fig. 5. — Mechanical stage to fit metallurgical microscope, magnetic specimen holder, and specimen.

flatter and more sharply defined images. The Zeiss projection eye-piece No. 2 is very satisfactory.

Iris Diaphragms. — Iris diaphragms are sometimes inserted between the objectives and the illuminator so as to control the size of the pencil of light proceeding from the object, with a view of securing sharper definition. Their use in that position, however, is of doubtful value, as it may cause some distortion of the image. It seems preferable to place the iris diaphragm between the source of light and the illuminator, thus regulating the amount of light entering the latter. When placed be-



Fig. 6. — Achromatic objectives.

tween the objective and the illuminator it increases, moreover, their distance apart, which we have seen to be objectionable. If a diaphragm must be attached to the microscope, it is better to place it between the tube nose and the illuminator. When using low-power lenses it might also be screwed to the lower end of the objective, thus controlling the light returned by the object *before* entering the objective.

Specimen Holders. — In order to examine a piece of metal under the microscope, it is of course necessary that the polished and otherwise prepared surface be held in a plane accurately perpendicular to the optical axis of the instrument. This may be

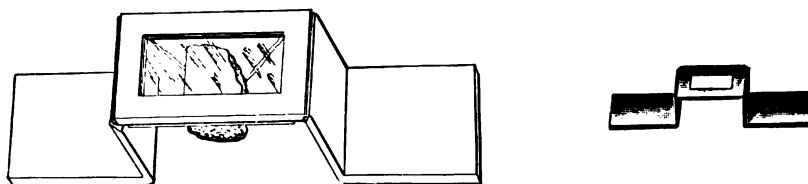


Fig. 7. — Specimen holder.

accomplished by so shaping the sample that it will have two sides exactly parallel, and preparing one of them for microscopical examination. This operation, however, is at best tedious and laborious, and metallographists have endeavored to replace it by the use of more or less ingenious devices for holding the specimens in the proper position. Some embed their samples in wax or in some other plastic material, while others have recourse to stages provided with special leveling devices.

The simple holder shown in Figure 7 gives better satisfaction, requiring no mounting whatever of the samples. The specimen, no matter how irregular in shape, is

held firmly in place by a rubber band and the holder placed on the stage like an ordinary slide. If the correction of the objective demands it, a cover glass may be inserted between the sample and the holder. It will be apparent that the required manipulations are very simple and quickly performed.

In the case of specimens smaller than the opening of the holder, however, the use of a cover glass is necessary to hold them in place. This is objectionable, at least when using high-power objectives, which should be corrected for uncovered objects. To overcome this difficulty, a little templet may be used having a triangular opening and inserted between the specimen and the holder (Fig. 8). This templet is made very thin so as to permit the use of high-power objectives, which must be brought very close indeed to the object. It will also be noticed that one side of the upper part

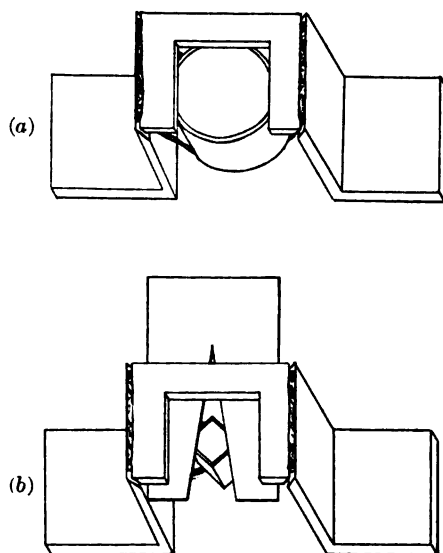


Fig. 8. — (a) Specimen holder and large specimen.
(b) Specimen holder, templet, and small specimen.

of the holder has been removed, exposing to view a larger portion of the sample and permitting a more ready approach of high-power objectives. Large samples are, of course, placed in the holder without any templet.

A still simpler and more effective device can be used to hold in place samples of iron and steel and other magnetic substances. The device consists of a V-shaped permanent magnet of special steel about 1 inch wide and $2\frac{1}{2}$ inches long (Fig. 9). This little magnet is placed on the stage of the microscope like an ordinary glass slide (Figs. 4 and 5) and the samples to be examined suspended to it from below, being held in place by the attraction of both poles. Small samples are suspended near the small end of the V-shaped opening, while larger ones are placed nearer the wider end of the opening. This holder, therefore, is universal in its application within the limits of samples of suitable size for microscopical examination. Its beveled edges make its use possible with high-power objectives and small specimens. If the opening of the stage be sufficiently large, say $1\frac{1}{4}$ inches or more in diameter, the magnet may be

kept permanently on the stage, as the samples may then be readily removed or attached to the magnet with the fingers from below the stage. This adds so much to the convenience of this little device that it is strongly urged, in case the central aperture of the stage is too small, to have it suitably enlarged. The magnet is kept in place, like any glass slide, by the clips of the microscope and, also like any glass slide, may be moved about for the inspection of the different parts of the specimen. The side of the magnet resting on the stage having been ground perfectly flat, it will be

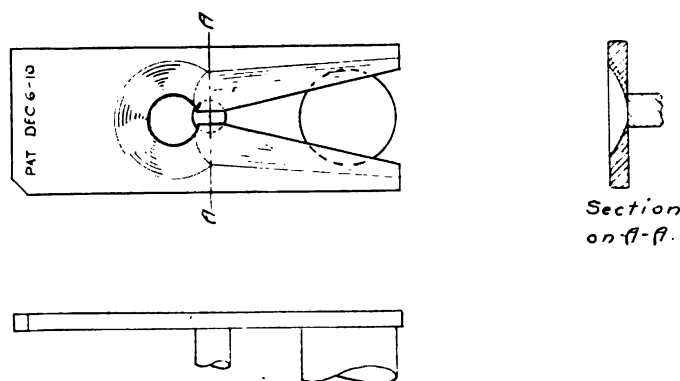


Fig. 9. — Magnetic specimen holder with large and small specimens.

evident that the surface of the sample under examination will always be accurately in the proper position, permitting the use of high-power objectives without fear of difficulty arising from ever so slight an inclination of the sample.

When used in connection with a mechanical stage (Fig. 5) the convenience of this little holder becomes still more apparent and its usefulness is further increased. It then affords, moreover, a ready means for the repeated examination of the same spot of any sample at any time. To that effect the holder is laid upon the prepared surface

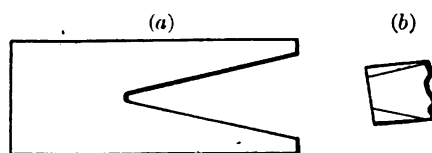


Fig. 10. — (a) Magnetic specimen holder.
(b) Scratched specimen.

and two scratches made by drawing a needle across the specimen along the sides of the V-shaped opening, as shown in Figure 10. When it is desired to examine the sample, the latter is suspended to the magnet so that the needle markings coincide closely with the sides of the magnet opening, in this way securing a permanent position for the sample. The position of the magnet itself is controlled, in the usual way, by means of the graduating devices of the mechanical stage.

Finally, by placing the sample below the stage and bringing the prepared surface

on a level with the stage, considerably greater working distance is secured, a gain which has its importance.

ILLUMINATION OF THE SAMPLES

Opaque objects such as metals and alloys must necessarily be examined by reflected light, i.e. by light thrown upon them from above the stage, their treatment differing in this respect from that of other microscopic preparations, which are generally examined by transmitted light, i.e. by light sent through them and proceeding from below the stage.

With low-power objectives there are two possible ways of illuminating opaque specimens: (1) by directing the light obliquely upon the object, and (2) by causing the light to fall perpendicularly upon it by means of so-called "vertical illuminators." With medium-high and high-power objectives the second method only is possible, because the distance between the specimen and the front lens of the objective is now

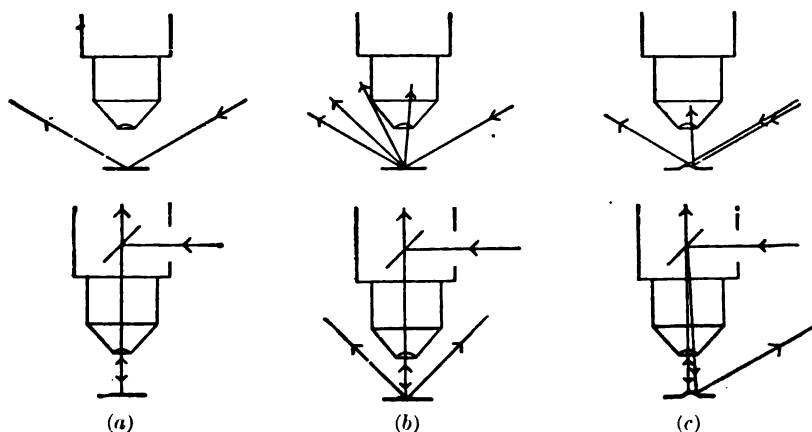


Fig. 11. — (a) Oblique and vertical illuminations of bright surface.
(b) Oblique and vertical illuminations of dull surface.
(c) Oblique and vertical illuminations of hills and valleys.

so small that obliquely reflected light cannot reach the surface under examination. With very low-power objectives — i.e. having a focal length of 1 inch or more — the vertical illuminator may be placed between the lens and the object; but with higher power objectives it must of course be inserted between the objective and the microscope tube, the objective then acting as a light condenser and increasing the intensity of the illumination.

Oblique illumination may be obtained (a) by allowing daylight or artificial light to fall freely upon the object; (b) by directing the light upon the object by means of mirrors, reflectors, or condensers; (c) by the use of a "lieberkühn"; and (d) by the use of a "parabolic reflector."

Vertical illumination may be produced (a) by means of an opaque reflector consisting of a totally reflecting prism or of a mirror covering only a portion of the objective, the light returned by the object reaching the eye by passing through the uncovered portion; and (b) by means of a transparent reflector, generally a plain

glass disk or glass square, reflecting upon the object a portion of the incident light and permitting the passage of a portion of the light returned by the object, which thus reaches the eye.

When a highly polished surface is examined by obliquely reflected light, since the angle of reflection is equal to the angle of incidence, the totality of the light is reflected outside the objective (Fig. 11) and the object appears uniformly dark. In case the metallic specimen contains some portions duller in appearance, these will scatter a certain amount of light a part of which will enter the objective (Fig. 11), and those portions will therefore appear brighter. A similar effect is produced when the specimen, instead of being perfectly flat, contains microscopic hills and valleys, the sides of which may be so inclined as to reflect some light into the microscope (Fig. 11), consequently appearing bright. Viewed by oblique light, therefore, the relative darkness or brightness of a constituent will vary inversely with its true appearance and

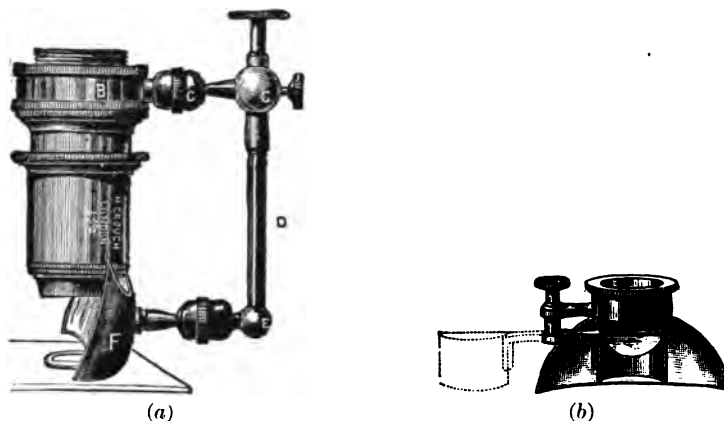


Fig. 12. — (a) Parabolic reflector.
(b) Sorby-Beck parabolic reflector.

will also depend upon its orientation, since this will affect the angle of incidence of the light striking it. Generally speaking, the darker a constituent the brighter will it seem to be when illuminated by oblique light, the latter yielding, so to speak, a negative image. Oblique illumination, moreover, cannot be made as intense as vertical illumination and, as already explained, is possible only with low-power objectives. For these and other reasons, while it is not without value, it is only used occasionally by metallographists.

To increase the intensity of oblique illumination and to make its use possible with somewhat higher powers, such appliances as the "lieberkühn" and the parabolic reflector have been used. The "lieberkühn," so called from the name of its inventor, consists of a small concave mirror attached to the objective and reflecting upon the object some light proceeding from below the stage and passing around the object. It will be evident that only small size objects can be thus illuminated.

The parabolic reflector (Fig. 12), first constructed by Messrs. Beck of London for Dr. Sorby, consists of a parabolic mirror placed on one side between the objective and the object and condensing the incident light upon the latter. It should be attached to the objective. Dr. Sorby later added a silver mirror in the shape of a half

disk to the same mount, so as to be able to obtain at will vertical and oblique illumination when using low-power objectives (Fig. 12). When vertical illumination is desired, the small mirror is swung over the objective, covering only a portion of it, and directing vertical rays of light upon the object. This combination is known as the Sorby-Beck reflector.

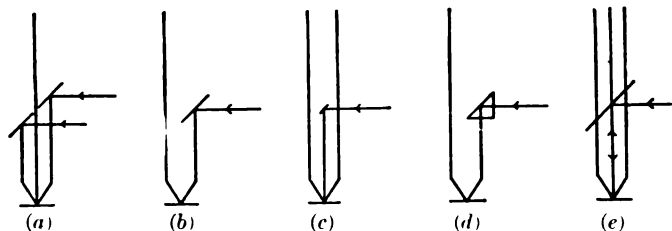


Fig. 13. — (a) Annular mirror.
(b) Semi-circular mirror.
(c) Central mirror.
(d) Totally reflecting prism.
(e) Plain glass disk.

The effects of a vertical illumination are precisely opposite to those of an oblique illumination, as clearly shown in Figure 11, highly polished surfaces reflecting the totality of the light into the objective, while dull ones appear dull because they reflect most of the light outside.

To produce a vertical illumination we have the choice between an opaque or a transparent (glass) reflector. The opaque reflector consists of a totally reflecting right-angled prism, or of a mirror placed between the microscope tube and the objective and covering only a portion (generally about one half) of its aperture. The beam

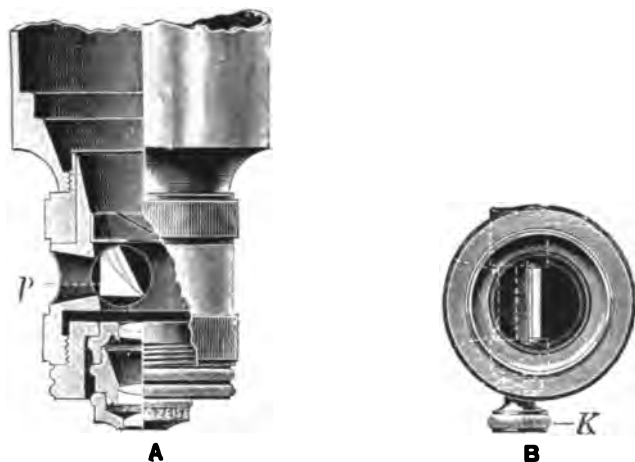


Fig. 14. — Vertical illuminator. Totally reflecting prism. (Zeiss.)

of light enters the illuminator through a side opening provided for that purpose and is reflected downwards by the reflector, being condensed upon the object by the lenses of the objective itself. The light sent back by the object reaches the eye through the uncovered part of the objective.

The first vertical illuminator was designed by Prof. Hamilton L. Smith of Hobart College, Geneva, N. Y., and consisted of a small annular silver mirror (Fig. 13), forming an angle of 45° with the axis of the microscope, the light reflected by the object passing through the central opening on its way to the eye. Semi-circular mirrors, similarly mounted and partially covering the objective (Fig. 13), have been used with equal satisfaction, and the author has obtained good results with

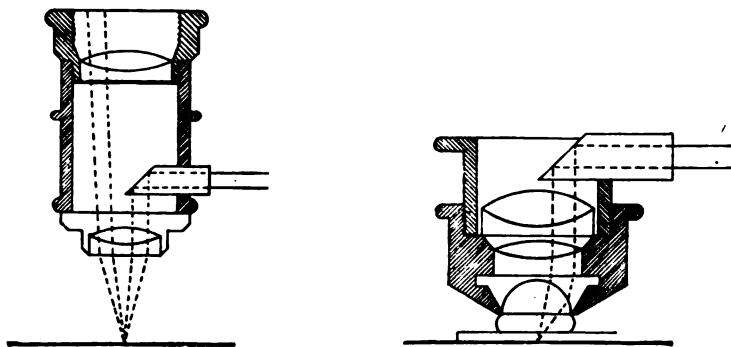


Fig. 15. — Nachet illuminating objectives.

a very small central mirror (Fig. 13) suitably mounted, reflecting the light upon the central portion of the objective lenses, and permitting the returned light to reach the eye through the free space surrounding the mirror.

Instead of a mirror, a totally reflecting right-angled prism may be used as shown in Figures 13 and 14, covering half of the aperture of the objective. The prism is so mounted that it can be rotated around its horizontal axis, this being needed in order to secure the best illumination of the sample. Nachet of Paris provides his prism



Fig. 16. — Bausch and Lomb plain glass disk vertical illuminator.

with an additional motion permitting it to cover a greater or smaller portion of the objective. These reflecting prisms are now used much more than the reflecting mirrors.

In 1874 Nachet constructed for the International Commission of the Meter some objectives provided with totally reflecting prisms as permanent parts of their mountings. In low-power objectives a prism was placed above the first lens (Fig. 15), while with higher power objectives it was necessarily inserted above the double or triple

lens system. These objectives are called illuminating objectives. This arrangement, however, has not been found very satisfactory and with one notable exception is seldom used by metallographists.

In vertical illuminators having a transparent reflector, the latter consists of a plain glass disk covering the whole of the aperture of the objective (Figs. 13 and 16). The incident light is in part reflected upon the object, while another portion passes freely through the glass reflector. A part of the light returned by the object is again reflected by the glass illuminator, while another portion passes through it and thus reaches the eye. The glass reflector is so mounted that it can be rotated around its horizontal axis (Fig. 16). The amount of light permitted to enter the illuminator may be regulated by an iris diaphragm attached to the side opening or independently mounted and placed between it and the source of light, or by a revolving sleeve attached to the illuminator and provided with different size openings. The first plain glass illuminator was constructed by Mr. Beck of London.

With very low-power objectives it is preferable to place the vertical illuminator between the objective and the object, attaching it to the former in some suitable way, as for instance by providing the lower end of the objective with a society screw (see Fig. 6).

While the author is well aware that some metallographists of note prefer the prism to the plain glass type of vertical illuminator, in his opinion the plain glass reflector is greatly superior. While the illumination obtained by its use is not quite as intense, it is certainly more uniform and less liable to produce a distortion of the image.

An improved construction of the plain glass vertical illuminator is illustrated in Figure 16. The glass reflector is inserted into a brass ring which on the side opposite the milled head is screwed into the wall of the brass mounting, practically doing away with the frequent breaking of the glass and greatly facilitating its cleaning. The milled head is large, which makes it possible to impart a more delicate motion to the glass reflector.

A more recent model designed by the author and made by Bausch and Lomb has an additional aperture opposite the opening where the light enters. This is for the purpose of preventing internal reflections from the walls of the illuminator by affording a means of exit for the light passing through the plain glass reflector. The same model has two opposite milled heads instead of one, attached to the ring mount which holds the reflector disk, thus increasing the convenience of its adjustment. There is also a small adjustable double convex condenser and iris diaphragm (see Fig. 28) attached to the aperture which faces the source of illumination. The condenser forms part of the condensing system of the illuminating system as explained later. The iris is useful in centering the beam of light, and increases the resolving power of the microscope at high magnifications.

Another recent model has a plain glass disk and two small central backed mirror reflectors, all interchangeable. It is also equipped with a condensing lens attached to the single aperture, but has no iris diaphragm. The backed mirrors are useful in micro-projection, but two have to be furnished: one for low and medium powers, and a smaller one for higher powers. Like the prism they do not give true vertical illumination, but a slightly oblique illumination is made necessary in order to avoid shadows in the image from the reflector itself; hence a slight relief effect. Like the prism the backed mirror produces a slight distortion of the image in photomicrography similar to that produced by lack of sharp focusing.

Vertical Magnifier. — For the examination of specimens after the polishing operation in order to ascertain the absence of scratches, for the examination of fractures, etc., and more especially for the measurement of the diameters of the spherical depression of the Brinell test for hardness, the “vertical” magnifier, Figure 17, has

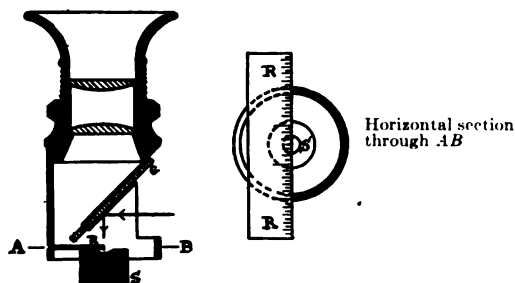


Fig. 17. — Vertical magnifier.

been found very useful. The plain glass reflector *G* placed at an angle of 45° causes the specimen under examination to be brilliantly lighted by vertical light as in the vertical illuminator attached to metallurgical microscopes. For the measurement of small distances (as in the Brinell hardness test), a thin steel scale *R*, with proper graduations, is inserted in a slot *A* cut in the mounting and so placed that the graduated edge meets the optical axis of the lenses.

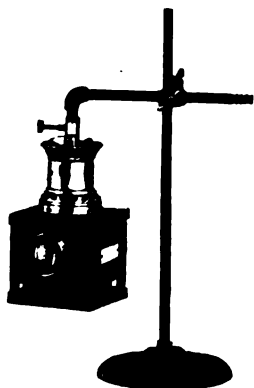


Fig. 18. — Welsbach lamp.



Fig. 19. — Mazda lamp.

SOURCES OF LIGHT AND CONDENSERS

The illumination of opaque objects such as metals and alloys requires an intense source of light, especially for their photography. Daylight and ordinary gas or oil flames should be discarded as not suitable for the purpose, the sources of light which have been found most satisfactory being, in the order of their excellence, intensity, and decreasing cost: (1) the electric arc lamp, (2) the gas-filled electric filament lamp, and (3) the Welsbach gas lamp.

The Welsbach lamp outfit (Fig. 18) is very inexpensive and quite satisfactory for visual examination by low- and medium high-power objectives. In taking photomicrographs, however, their lack of intensity necessitates very long exposures, while with high-power objectives the light received upon the camera screen is so faint as to render proper focusing of the object a very difficult, if not impossible, operation.



Fig. 20. — 6-volt Mazda lamp.

The author has used with considerable success, especially for visual examination, a gas-filled condensed filament lamp as shown in Figure 19, consuming either 100, 250 or 400 watts, depending upon the rating of the bulb which is of the stereopticon type. It is especially useful for illuminating simultaneously from four to eight microscopes



Fig. 21. — Details of 6-volt Mazda lamp supplied as alternative for arc lamp shown below on photomicrographic apparatus illustrated in Figs. 26, 27, 29, 30, 32, 37.

grouped about in a circle, for class use. It is generally used in connection with a double convex condensing lens mounted on a separate adjustable support.

Another electric filament lamp which has given satisfactory results both in visual work and in photomicrography when properly mounted (Fig. 21) is shown in Figure 20. It is of the automobile headlight type, and is generally mounted with a bi-convex condensing lens, consumes about 24 watts and by means of a small transformer (for



Fig. 22. — Details of arc lamp and condenser housing and aspheric condenser generally forming part of photomicrographic apparatus illustrated in Figs. 26, 27, 29, 30, 32, 37.



Fig. 23. — Arc lamp on separate adjustable support equipped with small bull's-eye condenser.

alternating current) or a rheostat (for direct current) can be connected to any 110- or 220-volt circuit. It gives a steady light and is economical of current. When suitably mounted with an aspheric condenser as in Figure 21, it is especially convenient when the operator is working steadily for long periods and in photomicrography at low and medium magnifications, although the exposures are necessarily long.

Nernst filament, oxyhydrogen, and acetylene lamps were formerly used to some extent but have now been pretty generally superseded.

Arc lamps consuming from 15 to 25 amperes (1650 to 2750 watts) were formerly used extensively in photomicrography but they have gradually given place to a quiet-running $4\frac{1}{2}$ -ampere arc lamp illustrated in Figures 22 and 23.

The 15-ampere lamp required carbon electrodes from $\frac{1}{16}$ to $\frac{1}{8}$ inch in diameter and were generally used in connection with a triple condensing system and cooling cell similar to that illustrated in Figure 24. The present lamp uses carbon electrodes about $\frac{1}{8}$ inch diameter, and is generally mounted with an aspheric condenser to be described later and illustrated in Figure 22. It can be stepped up to 10 or even 15 amperes by means of a special rheostat for obtaining greater intensity for short periods where the specimen is dark or lacking in contrast or detail. No cooling cell is necessary, but the higher currents must be used with great caution and not long at a time, or injury may be done to the objective lenses or ray filters. In all arc lamps the car-

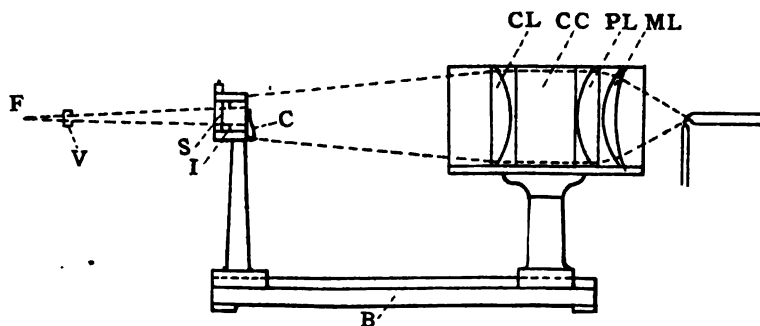


Fig. 24. — Condensing lenses, *CL*, *PL* and *ML*; cooling cell, *CC*; iris diaphragm, *I*; automatic shutter, *S*; and optical bench, *B*.

bons should be placed at right angles, as this arrangement directs the maximum amount of light into the condensers. Both carbons should be cored and for direct current the vertical or negative carbon should be smaller than the horizontal carbon. Automatic feeding of the carbons is not by any means essential, as remarkably effective hand-feed lamps are now constructed by which a very steady light can be maintained (Fig. 22). Automatic mechanisms, moreover, are liable to get out of order and occasional sudden shiftings of the light are difficult to eliminate entirely.

The recent lamps are much less expensive than their larger predecessors, but the intensity is not reduced to an inconvenient extent. In taking photomicrographs the exposures generally vary between 5 and 60 seconds, depending upon the kind of current, the magnification, the adjustment of the condensing system and the relative brightness or darkness of the object.

The positions of the carbons on the modern arc lamp can be regulated with great nicety by independent adjustments, thus securing a very uniform light lasting from 6 to 9 minutes before a new adjustment is required.

Summing up, if we desire a cheap and convenient form of illumination for visual examination with objectives of low- and medium-high power, the Welsbach lamp will be found in every way satisfactory; while for the taking of photomicrographs and for examination by high-power objectives the electric arc lamp, the 6-volt Mazda, or the 250 or more watt, gas-filled, Mazda lamp should be recommended.

Condensers. — Some kind of condensing attachment must be placed between the source of light and the vertical illuminator so that a large portion of the light may be

utilized and a beam of suitable size directed into the illuminator. In the case of light proceeding from a luminous point or at least from a small luminous area, as for instance with the electric arc, at least two lenses or systems of lenses are needed, one system placed near the source of light, to collect the divergent rays and convert them into a parallel beam, and a second lens placed at some distance from the first, to convert the parallel beam into a converging one. The vertical illuminator should be located at such a distance from the condensing lens that the beam of light will cover a little more than the opening through which it enters the illuminator. With arc lamps using more than 5 amperes a glass cooling cell, filled with distilled water or some other suitable liquid, should be placed between the two lenses in order to absorb a large amount of the heat and thereby prevent injury to the objective. An iris diaphragm should also be used to control the amount of light entering the vertical illuminator. This diaphragm should be placed in front of the converging lens and may be provided with clips for holding ground and colored glasses. These various parts should be mounted on a so-called "optical bench" upon which they can slide.

With a large luminous body such as the Welsbach mantle, a bull's-eye condenser (planoconvex), (Fig. 18), is sufficient to collect and condense the necessary amount of light. It should, of course, be placed at the proper distance both from the vertical illuminator and from the source of light. The use of an iris diaphragm attached to the vertical illuminator or on a separate mount is advisable, since it affords a ready means of controlling the amount of light admitted into the illuminator.

In Figure 24 is shown the triple condensing system formerly used with 15-ampere arc lamps and 400-watt gas-filled Mazda lamps. This consisted of a meniscus or collecting lens, *ML*, a planoconvex or parallelizing lens, *PL*, and a condensing lens, *CL*, and the approximate course of the beam is shown by the broken lines in the illustration. *C* is the spring clip for holding ray filters, *I*, the iris diaphragm, *S*, the automatic shutter and *V* the vertical illuminator in proper relation to *F*, the focal point of the light rays.

This large and rather awkward system has now been quite generally replaced by the so-called aspheric system (duplex).

In photomicrographic work, the spherical correction of the condensing lens used in connection with the illuminating outfit is an important point to be considered. The aspheric condenser now usually supplied with all photomicrographic outfits described in this chapter was designed with this in mind. It is corrected for spherical aberration by grinding to non-spherical curves. By means of this correction, an image of the arc is formed practically in one plane, so that a much greater percentage of the light collected from the arc may be utilized than with the older spherical condensers (triple systems). The focus of this aspheric lens is such that it takes in a cone of light from the arc lamp of about 60° and forms a large image of the arc. The lens itself is 60 mm. ($2\frac{3}{8}$ in.) diameter. The beam of light after passing through the condenser is nearly parallel when the condenser is properly placed, so an auxiliary condenser is attached by means of a tube to the vertical illuminator. An iris diaphragm is generally attached to this tube between the aspheric condenser and the auxiliary condenser, the latter being adjustable horizontally in the tube. The aspheric condenser is fitted in a spiral focusing mount and may be used either with the $4\frac{1}{2}$ -ampere arc or the 6-volt Mazda lamp interchangeably as shown in Figures 21 and 22. The housing of the aspheric condenser is very compact and is generally fitted with means for holding ray filters as shown in Figures 21 and 22.



Fig. 25. — Photomicrographic camera showing metallurgical microscope, mechanical stage, automatic shutter, etc.

Monochromatic Light. — The different lamps described above all yield, of course, white light, and since the correction even of apochromatic objectives for chromatic aberration is never perfect, it is evident that the use of monochromatic light — i.e. light of one wave length — is preferable, especially for photographing. Monochromatic light may be obtained in two ways: (a) by using a source of light actually monochromatic, and (b) by causing white light to pass through colored glass screens or colored solutions (light filters), preventing the passage of some undesirable rays. The mercury arc lamp yields a nearly monochromatic light and has been tried by Le

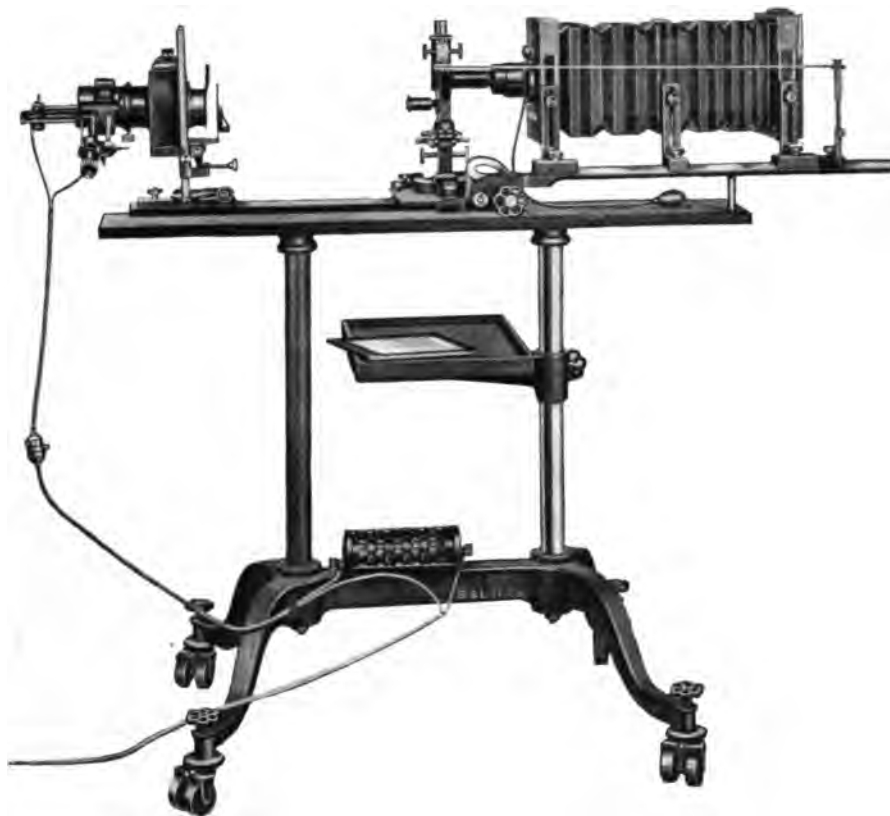


Fig. 26. — Photomicrographic apparatus with vertical microscope, permanently connected horizontal camera, arc lamp and aspheric condensing system rigidly mounted on heavy iron table.

Chatelier with satisfactory results. It seems more convenient, however, when monochromatic light is wanted, to use light filters of suitable colors, in which case colored glass screens will be found easier to manipulate than glass cells containing colored solutions.

Green is the color for which most achromatic objectives are corrected, and filters of this color increase the clearness and detail of the image in a wonderful manner in photomicrography. Some prefer a medium shade of yellow for the filter. The screen in either case should be in place during focusing of the image and during the exposure. It is necessary, of course, to use an orthochromatic or pan-

chromatic plate if the best results and shortest exposure are desired. A bright red screen is often used in photomacrography and must be used with a panchromatic plate sensitive to red light. This combination gives a maximum of detail and contrast.

PHOTOMICROGRAPHIC OUTFITS

For taking photomicrographs, a light-tight connection should be established between the microscope and a suitable (Fig. 25) camera.

The arrangement the author has found by far the most satisfactory is illustrated in Figure 26. The microscope is similar to that shown in Figure 1 but has a second



Fig. 27. — Photomicrographic outfit with camera in vertical position.



Fig. 28. — Showing details of special microscope and vertical illuminator with auxiliary condenser, all forming part of the apparatus shown in Figs. 26, 27 and 29.

body tube in a horizontal position, sliding with a slot and pin arrangement, and fitted at the inner end with a totally reflecting prism, which, when the tube is pushed in, causes the beam of light to turn at 90° and enter the permanently connected horizontal camera shown in the illustration.

The microscope, camera, and illuminating system are mounted on the same rigid support, thereby securing accurate alignment, freedom from vibration, and easy manipulation.

Plates measuring 5×7 inches and smaller may be used. The source of light is an electric 90° arc lamp (or 6-volt Mazda lamp), supplied with the aspheric condensing system, with a lens 60 mm. in diameter. The current may be direct or alternating. The lamp is enclosed in a small cylindrical hood with observation windows. The carbon adjustment can conveniently be reached by the observer at the microscope. Clips fastened to the front of the condenser housing permit the use of monochromatic glass screens, ground glass, etc. The light can be quickly tilted at any desired angle

for transparent or for oblique illumination. In Figure 27 is shown the same outfit with camera in vertical position.

Figure 28 shows the details of the special microscope and improved form of plain glass vertical illuminator used with it.

In Figure 29 is seen the same microscope attached to an 8×10 camera.

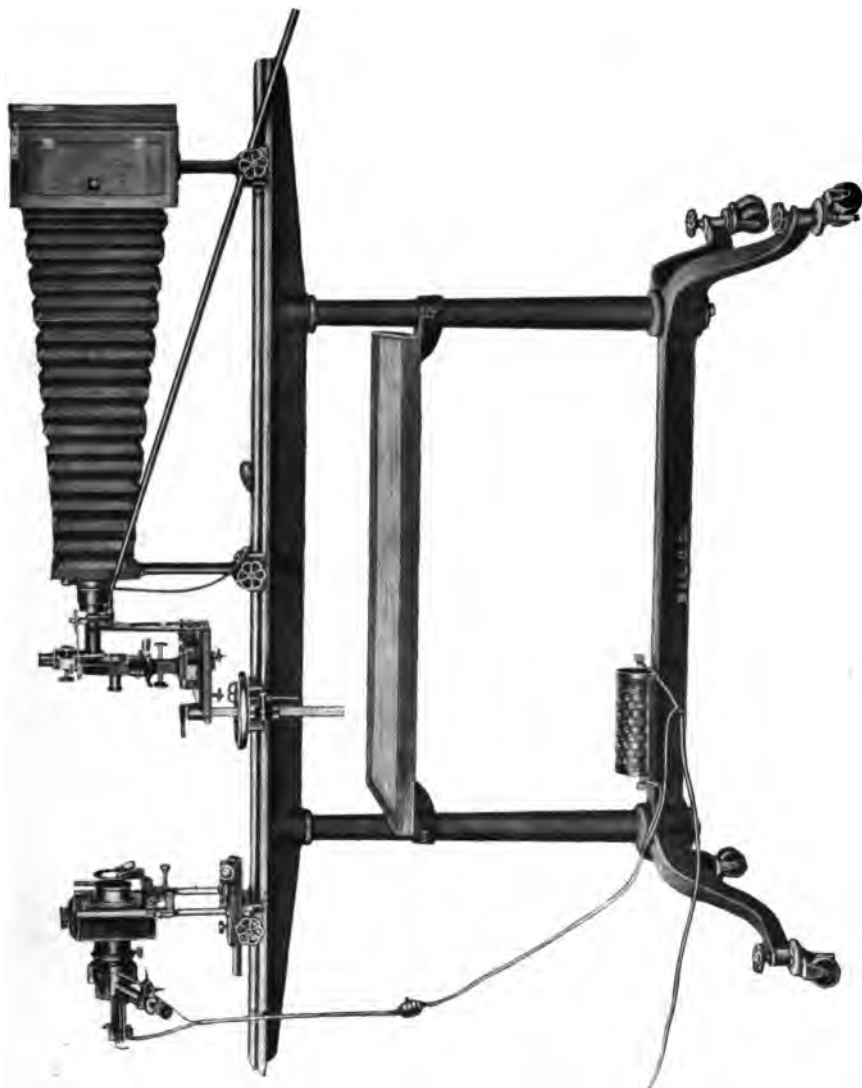


Fig. 29. — Photomicrographic apparatus similar to that shown in Figure 26 but with 8×10 camera and heavier iron table.

Figure 30 shows a somewhat simpler form of this apparatus using the regular microscope illustrated in Figure 1. The supporting table is of such a height that the observer may be seated (Fig. 31*b*), for visual work and in a comfortable standing position (Fig. 31*a*), for the focusing of images on the screen of the camera. Connection between the microscope and camera is very quickly and easily made. Plates measuring 5×7 inches and smaller sizes may be used. It is equipped with the same lamp and condensing system as the outfit previously described.

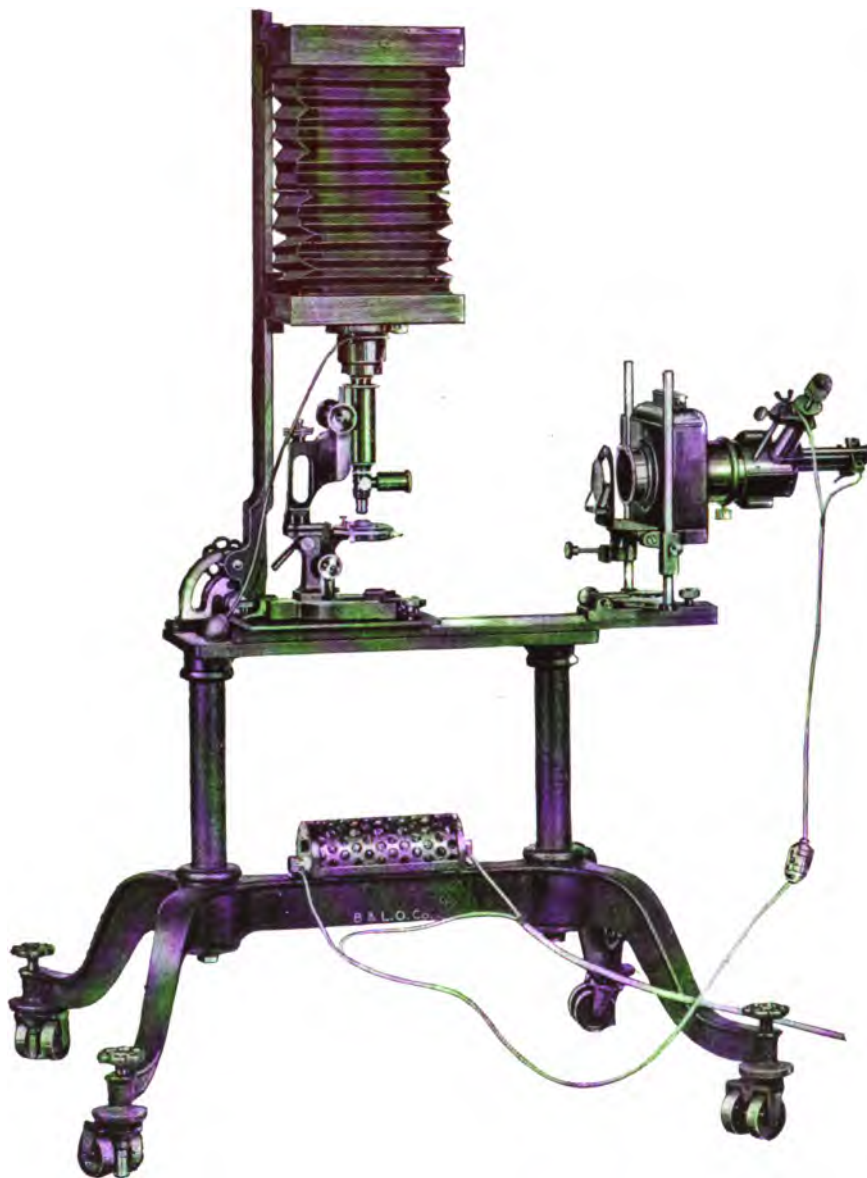


Fig. 30. — Vertical microscope with arc lamp and vertical camera mounted on heavy iron table.

INVERTED MICROSCOPES

Le Chatelier was the first to suggest the use of an inverted microscope for the examination of metallic surfaces. In this style of microscope the stage is placed horizontally *above* the objective, the latter being necessarily pointed upwards (Figs. 32 to 37).

In the inverted type of microscope and photographic attachment illustrated in these pages, it has been attempted to simplify the construction with corresponding material decrease in price.



Fig. 31a. — Position for photomicrography.



Fig. 31b. — Position for visual examination.

The microscope is *permanently* connected with the camera by a totally reflecting prism P (Fig. 34) set rigidly below the vertical illuminator. A separate tube set at 180 degrees to the first is provided for visual examination, another totally reflecting prism P' being fastened to the inner end and serving to reflect the image from the body tube through the eye tube to the eye. When a photograph is to be taken this prism P' is simply withdrawn from the field by means of the draw tube. The eye tube is fitted with pin and slot which mark the limits to which the small prism P' may be pushed in and withdrawn, so that the vertical illuminator being once set, the only adjustment necessary is at the arc lamp. With the 6-volt Mazda lamp, after the light and the vertical illuminator are once set, no more adjustments are necessary. The two totally reflecting prisms need never be rotated and in fact cannot be moved, except for the sliding motion of the prism P' as already described.

The stage, which is revolving and provided with centering screws, is of course equipped with both coarse and fine adjustment, and a mechanical stage may readily be substituted for the plain stage.

With this inverted microscope the use of a magnetic holder will also be found very



Fig. 32. — Inverted metalloscope ($\frac{1}{9}$ actual size).

convenient, for the sample, instead of resting loosely on the stage, is then held firmly in place, thereby increasing the usefulness of the mechanical stage.

The placing of the light on the same side of the microscope as the camera makes it possible for the operator to regulate his illumination while focusing the object on the camera screen.

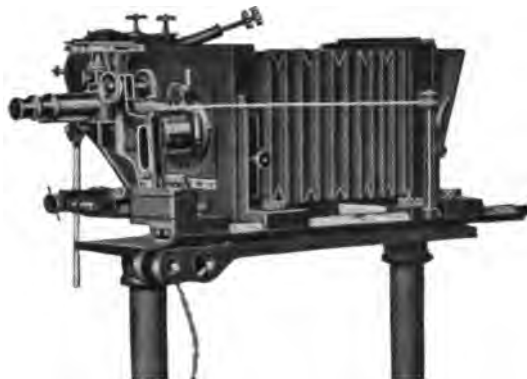


Fig. 33. — Inverted metalloscope (rear view). Showing means of controlling fine adjustment.

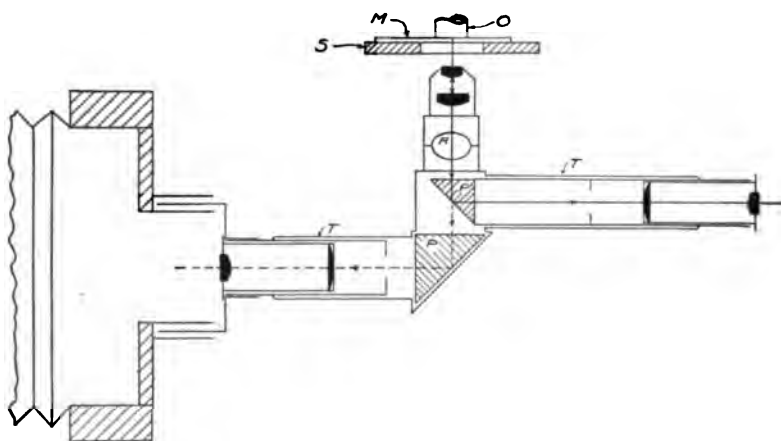


Fig. 34. — Inverted metalloscope (vertical section, front view).

R = Vertical illuminator reflector.

P' = Totally reflecting prism which reflects image into the eye tube when latter is pushed in.

P = Totally reflecting prism which reflects image into camera when eye tube is pulled out.

S = Metalloscope stage.

M = Magnetic specimen holder.

O = Specimen.

One of the valuable features of this model is its compactness. While at the camera screen, the operator can easily reach the lamp adjustments, and the fine adjustment of the microscope is controlled from the same position by means of a thread belt actuated by a small milled head pulley placed on a standard at the end of the camera bed bar near the screen (Fig. 33).



Fig. 35. — Heavy metalloscope with four-post stage.

A heavier and more rigid adaptation of the metalloscope is shown in Figure 35. The principal features of this model are: a stage, $4\frac{1}{2}$ inches square, is mounted on four posts on a base, attached to the upper end of the rack slide. The rack and pinion of the coarse adjustment is operated by a worm gear, which automatically locks when any downward pressure is put upon the stage. An extension rod and gears are provided for operation of the fine adjustment when observing an image on the camera screen. A special mechanical stage, as illustrated in Figure 36, is provided with a holder with spring clips for handling small specimens. The vertical illuminator is so arranged that either a clear glass or a totally reflecting small mirror may be used interchangeably in the same mounting. A side tube with adjustable condenser



Fig. 36. — Special mechanical stage, forming part of heavy metalloscope.

is attached to the mounting of the vertical illuminator. The end of the vertical illuminator receiving the objective is turned out with a slight taper, into which fits a taper ring screwed to each objective. This makes possible the quick interchange of objectives. Short-mounted objectives must be provided for use with the totally reflecting mirror, but these do not give as good results with the plain glass reflector as those in long mounts so that obviously two sets of objectives must be provided (one in short mount, and one in long) if the best results are to be expected, especially at high and medium-high magnifications. There is generally provided the arc lamp or the 6-volt Mazda lamp and aspheric condensing system described on page 23.

A camera for plates 8×10 inches or smaller is provided. The complete photomicrographic outfit is illustrated in Figure 37.

POLISHING APPARATUS

Hand Polishing. — When, in spite of the length and laboriousness of the operation, iron and steel samples are to be polished by hand, four smooth blocks of wood should be prepared, some 6 by 10 inches and 1 inch thick. Two of these should be covered with canvas or linen duck and the others with fine broadcloth. The blocks are to be used as described in Chapter II.

Polishing by Power. — The power polishing machine shown in Figure 38 has been found very satisfactory. It consists of a heavy iron pedestal upon which is mounted a grinder having emery-wheel and composition disks revolving in a vertical plane, thus giving four polishing surfaces of graduated fineness. The polishing powders mixed

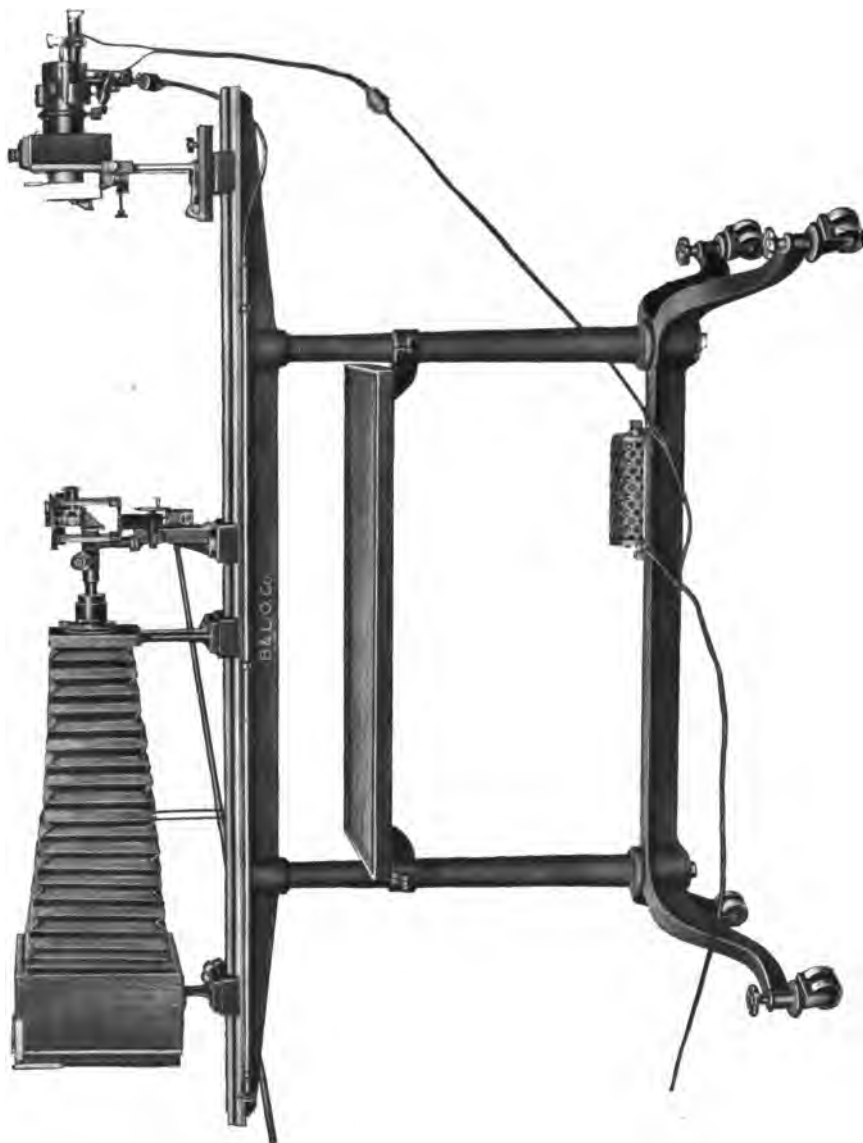


Fig. 37. — Complete photomicrographic equipment with heavy metalloscope and 8×10 camera.

with water are applied to the various disks by means of brushes, and shields are provided to catch any surplus water that may be thrown off during the operation. Should a cloth become worn or torn it is readily and quickly replaced. This machine very much shortens the time necessary for the preparation of samples and is far superior to those where only one block is made to rotate at a time. A speed of 1200 revolutions per minute has been found most satisfactory for polishing iron and steel samples,



Fig. 38. — Power polishing machine.



Fig. 39. — Polishing motor.

but by the use of a variable speed electric motor to run the polishing machine various speeds may be readily obtained.

The polishing motor shown in Figure 39 possesses the advantage of directly-driven over belt-driven machinery. It is provided with the same polishing disks as the polishing machine and can be built both for constant and for variable speed.

The operation of polishing with these machines is described in Chapter II.

Portable Polishing Motor. — A portable polishing motor is shown in Figure 40. It has been devised for the purpose of polishing small spots (about $\frac{3}{4}$ inch in diameter) on pieces too large to be treated in the ordinary way and from which samples of suit-



Fig. 40. — Portable polishing motor.

able dimensions cannot readily be cut, as for instance finished forgings or castings, etc. It consists of a $\frac{1}{8}$ -H.P. motor, flexible shaft, grinding heads, and polishing disks suitably covered. A spot may be satisfactorily polished in some 15 to 20 minutes.

PYROMETERS AND ELECTRIC FURNACES

Pyrometers. — The Le Chatelier thermo-electric pyrometer is undoubtedly the instrument best adapted to the measurement of temperatures needed to control such heat treatments as are likely to be performed in a metallographical laboratory. The

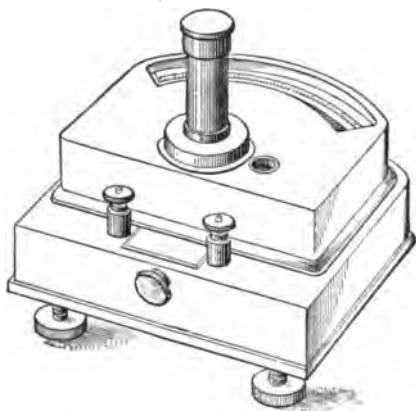


Fig. 41. — Siemens and Halske galvanometer.



Fig. 42. — Leeds and Northrup thermo-couple potentiometer.

thermo-couple consists of a wire of pure platinum and of a wire of platinum alloyed with 10 per cent of rhodium or iridium. To measure the electromotive force created, an accurate direct-reading galvanometer should be used (Fig. 41) or else the poten-

tiometer method (Fig. 42). Instructions for the use of these instruments are generally supplied by the makers.

The use of cheaper couples and cheaper instruments is not to be commended, for they are unsuitable for accurate scientific work especially at high temperatures.

An autographic recording pyrometer is very useful and quite indispensable for the detection of faint evolutions or absorptions of heat. Indeed without its use there are many delicate thermal treatments that could not be performed. Several autographic instruments are now constructed. To meet the needs of the metallographist the author believes that the pyrometric recorder designed by Le Chatelier and Sala-

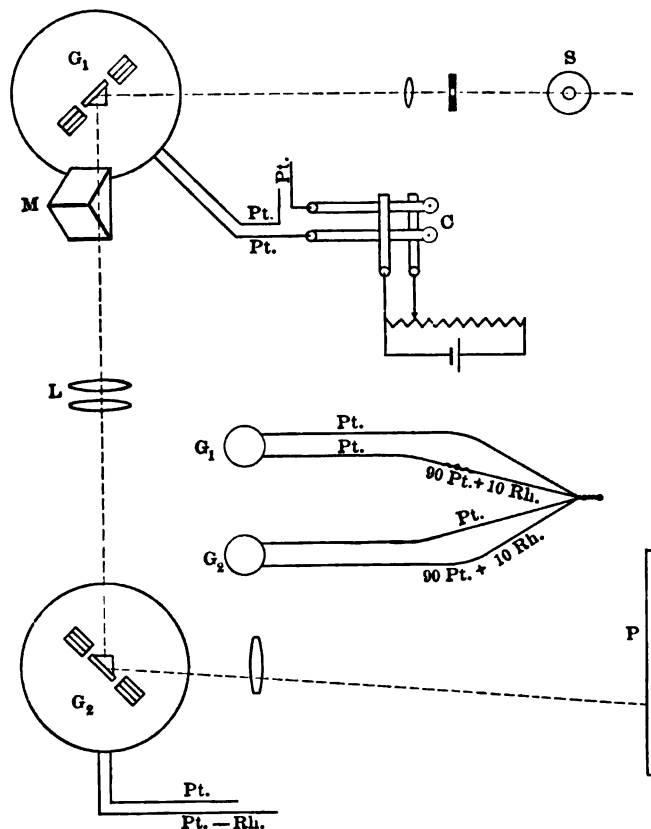


Fig. 43. — Saladin self-recording thermo-electric pyrometer.

din and constructed by Pellin of Paris (Figs. 43 to 45) will be found most satisfactory. In an early form the different parts were arranged as shown in Figure 43. The light proceeding from the source *S* after passing through a lens is received by the mirror of a sensitive galvanometer *G*₁ the deflections of which measure the difference in temperature between the sample under examination and the neutral body. This horizontal deflection of the beam of light is converted into a vertical deflection by passing through a totally reflecting prism *M* placed at an angle of 45 degrees.

This vertically moving beam of light is received by the mirror of a second galvanometer *G*₂ whose deflections are a measure of the temperature of the sample. The beam then passes through a lens and reaches the screen or plate *P*. *L* is a lens at the

conjugate foci of which are placed the mirrors of the two galvanometers. Two motions are in this way imparted to the spot of light, (1) a horizontal motion proportional to the temperature of the sample and (2) a vertical motion proportional to the difference in temperature between the sample and the neutral body. The resulting curves are known as differential curves (see Chapter X).

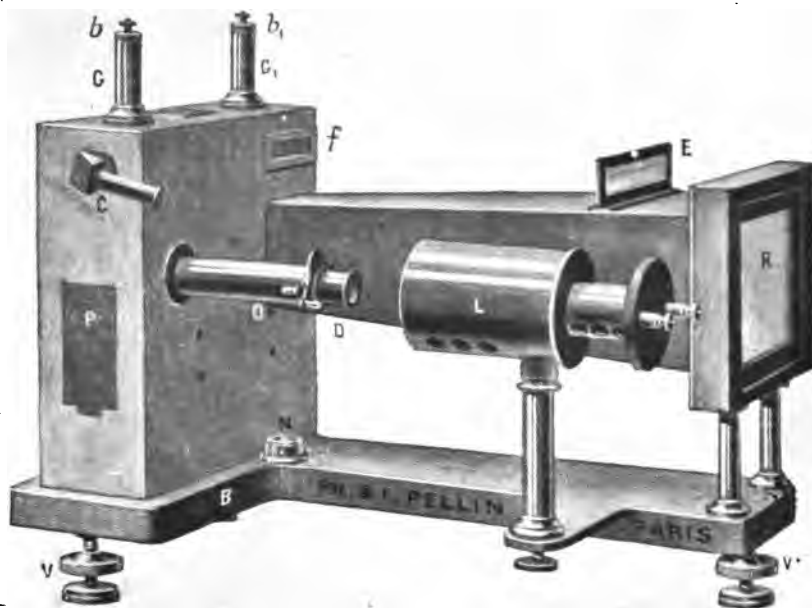


Fig. 44. — Le Chatelier-Saladin self-recording thermo-electric pyrometer.

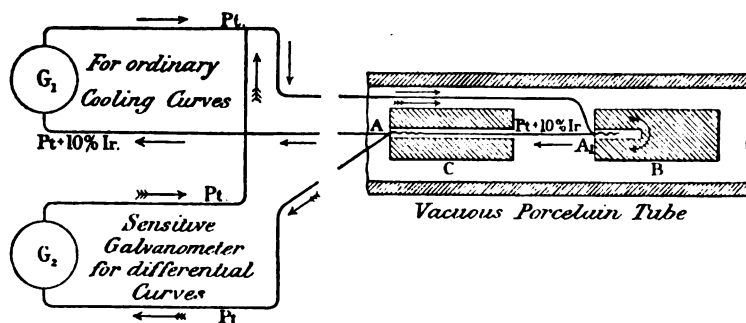


Fig. 45. — Roberts-Austen method of connecting the sample, neutral body, and galvanometers.

In recent models the apparatus has been simplified and made more compact (Fig. 44) by placing the galvanometers so near each other that the lens *L*, Figure 43, could be omitted and the entire instrument placed in a metallic or wooden case.

The apparatus is mounted on an aluminum base *B* provided with three leveling-screws *VV'V''* and a level *N*. The optical and electrical parts are enclosed in a vertical aluminum box. The suspensions of the galvanometers are regulated through

the milled heads bb_1 attached to the suspension wires. The light proceeding from the source at L (Nernst or incandescent lamp) fall on the collimator O provided with a diaphragm. D is the camera and R the screen. A small collimator C lighted by the source L throws its image on a small auxiliary mirror which projects through the slit F a luminous spot on the scale E , making it possible to follow from the outside the traveling of the luminous spot on the photographic plate during exposures.

The connections between the sample and the neutral body and between these and the galvanometers are made, as first suggested by Roberts-Austen, and as clearly shown in Figure 45. In this illustration galvanometer G_1 corresponds to galvanometer G_2 of Figure 43 and galvanometer G_2 to galvanometer G_1 .

ELECTRIC FURNACES

For the experimental treatment of small samples of iron and steel an electric resistance furnace is extremely useful. Satisfactory types of platinum-wound furnaces are supplied by makers. For temperatures not exceeding 1000 deg. C. furnaces wound with nichrome wire can be readily and cheaply built in any laboratory, both muffle and tube pattern. For very high temperatures (1200 to 1600 deg.) kryptol furnaces are to be recommended. When iron and steel samples are to be heated in vacuum, under pressure or in an atmosphere of various gases, special furnaces must be built provided with vacuum apparatus, pressure pumps, gauges, etc.

CHAPTER II

MANIPULATIONS

The author's manipulations are described in this chapter, at some length; others more briefly in Chapter III.

Cutting of Samples. — Samples of iron and steel for microscopical examination should not generally exceed $\frac{1}{2}$ inch square or round. If the metal is sufficiently soft they can be cut readily with a hand saw or, preferably, with a power hack saw. If too hard, emery disks or diamond saws should be used. Suitable pieces of hard, brittle metals (white cast iron, spiegeleisen, etc.) may sometimes be obtained by breaking with a hammer.

Polishing by Hand. — The outfit described in Chapter I should be used. The sharp edges of the sample should be filed or ground in order to avoid tearing the polishing cloths in the following operations. The surface to be prepared should be filed first with a coarse and then with a smooth file so as to obtain a perfectly flat, smooth surface. This filing can be advantageously replaced by grinding on a fine emery-wheel. It is recommended that both filing or grinding be conducted with a very gentle pressure.

A small amount of No. 80 emery-powder¹ mixed with sufficient water to form a thick paste should be placed on one of the polishing blocks covered with linen cloth. This paste should be spread over the block, conveniently by means of a spatula, and with the addition of a little more water if necessary. The sample of metal should now be rubbed back and forth over this block, being careful to rub always in the same direction until the marks left by the file or emery-wheel have all been removed and replaced by finer markings due to the action of the emery-powder. After this treatment the sample should be carefully washed, as well as the fingers of the operator, preferably in running water, and the sample rubbed over the second polishing block covered with linen cloth and a little flour-emery and water, precisely as before. On passing from the first to the second polishing block, the sample should be turned at right angles and kept in that position, in order that the new marks may be perpendicular to the old ones, and the polishing should be continued until the marks left by the coarse emery have been entirely effaced and replaced by finer ones. The sample after being carefully washed is ready for the next block. Some of the tripoli powder should be spread, with the addition of water, over one of the blocks covered with broadcloth, and the sample polished upon this block until the markings left by the previous polishing have been completely removed. After careful washing the sample should now be rubbed over the last polishing block, covered with broadcloth, rouge,² and water, holding as usual the sample so as to rub it at right angles to the markings left by the tripoli. After these markings have been removed the sample should have a very bright surface and be free from even microscopical scratches.

¹ The polishing powders should be of the very best quality obtainable.

² It is essential to use the best commercial grade of jewelers' rouge.

At this stage a magnifying-glass is very useful for inspecting the specimen in order to ascertain whether it is ready for the etching treatment. For this purpose the vertical magnifier described and illustrated in Chapter I will be found very satisfactory.

The specimen should now be carefully washed and dried with a soft cloth, preferably a fine piece of old linen. Where an air blast is at hand, as is generally the case in chemical laboratories, it is advisable to dry the specimen with this blast (a hot blast is more effective than a cold one) instead of rubbing it with a cloth. The sample may then be passed gently once or twice on a piece of chamois leather stretched over a smooth piece of wood and carefully protected from dust when not in use, when it will be ready for the next or etching operation. When polishing, the sample should be pressed lightly upon the blocks and great care taken not to carry any coarse powder over a polishing block upon which a finer powder is used, as the presence of but a few coarser grains will greatly lengthen the operation. It is of much importance, therefore, to keep all the blocks carefully covered when not in use as well as the bottles containing the powders.

Polishing by Power. — Polishing by hand is at best a tedious and laborious operation, and whenever possible it is highly advisable to replace it by the use of a power polishing machine. Very satisfactory and effective polishing machines and polishing motors have been described in Chapter I.

When using these polishing machines or polishing motors the manipulations are as follows:

The metal surface to be prepared is pressed lightly upon the emery-wheel until a perfectly flat surface is obtained, when it should be washed with the usual precautions and pressed upon the cloth-covered composition disk placed next to the emery-wheel and upon which flour-emery and water have been applied. Care should be taken to hold the specimen so that the new marks will cross the old ones at right angles, and the grinding should be continued until the emery-wheel marks have been completely erased. After washing the specimen it is ready for treatment on the next surface covered with broadcloth upon which has been spread tripoli powder and water, here again turning the sample 90 degrees. When the marks left by the preceding operation have been removed, the specimen is washed and given the final polishing treatment by pressing it lightly upon the other side of the composition disk upon which rouge and water is used. The various polishing powders mixed with water may be conveniently applied to their respective disks by means of flat and rather stiff brushes. The surface of a properly polished sample should be highly specular and free from scratches.

Time will be saved by exerting a slight pressure only while polishing, especially on the emery-wheel and emery-disk, because deep marks due to these abrasers will be troublesome to remove with the finer powders. With these machines a sample of steel measuring $\frac{1}{2}$ inch square or $\frac{1}{2}$ inch in diameter is readily polished in 10 minutes.

Polishing very Small Specimens. — For the polishing of samples too small to be conveniently held in the hand and also for preventing the rounding off of the edges the author following Boylston's suggestions uses small iron caps, known in the trade as "malleable gas caps," in two sizes, namely, $\frac{3}{8}$ inch and $\frac{1}{4}$ inch. — They cost three to four cents each.

The cap used as a crucible is heated to about 200 deg. C. by placing it on an iron plate heated by a Bunsen burner. It is then filled with a fusible alloy recommended by Campion and Ferguson and consisting of 50 parts bismuth, 30 parts lead, 25

parts tin, and 3 parts zinc. This alloy melts below 100 deg. C. and if used in stick form, the heated iron cap can readily be filled with molten alloy. The temperature of the cap and its contents is kept a little above 100 deg. C. and the specimen to be polished pressed into it. After solidification and cooling, which can be hastened by dipping in water, the whole is polished in the usual way.

By using iron caps instead of brass cylinders or other non-magnetic mounts the magnetic holders described in Chapter I can be used with great gain in simplicity and convenience.

Etching. — If the polished samples were now placed under the microscope it would be possible to detect the presence of inclusions such as graphite particles, slag, etc., and if a relief effect has been produced, the presence of constituents considerably harder than the matrix (free cementite in hyper-eutectoid steel, for instance) but the structure of the metallic matrix itself would not be revealed, because its constituents being equally bright and exactly in the same plane would reflect the light to the same extent, after the fashion of a mirror. To make the structure apparent under the microscope it is necessary to impart unlike appearances to the constituents. This is generally accomplished by producing a slight corrosion or etching of the polished surface. For this purpose acid solutions are generally used which attack some constituents more deeply than others or to the exclusion of others, an action which may or may not be accompanied by the deposition of some precipitated matter.

Arnold considers the operation of etching with dilute acids to be of an electrolytic nature, some of the constituents being electro-negative to others, hence the attack of some of these (electro-positive constituents) to the exclusion of others (electro-negative constituents) and the darker coloration of the former.

For the development of the microstructure of polished samples of iron and steel in general, the author's preference is as follows: (1) solution of nitric acid in alcohol, (2) solution of picric acid in alcohol, and (3) concentrated nitric acid.

Nitric Acid and Alcohol. — A solution should be prepared containing 10 per cent of concentrated, chemically pure nitric acid and 90 per cent of absolute alcohol. A small amount of this solution should be poured in a glass or porcelain dish, preferably a small crystallizing glass dish with cover, and the sample immersed in it for 10 seconds, when it should be removed, conveniently with a pair of pincers (preferably with platinum tips), and washed in alcohol. The sample should now be dried, preferably by means of a blast for which a foot-blower will answer very well. After rubbing the sample *very gently* once or twice upon a smooth piece of chamois leather stretched on a wooden block and carefully kept free from dust, it will be ready for examination. In case the etching is not sufficiently deep the treatment should be repeated.

Picric Acid. (Igevsky.) — An etching solution should be prepared containing 5 grams of picric acid, chemically pure, and 95 cubic centimeters of absolute alcohol. This should be kept in a well-stoppered glass bottle. The samples should be immersed in it for 30 seconds, washed in alcohol, dried, and the treatment repeated if necessary.

Concentrated Nitric Acid. (Sauveur.) — The polished specimen conveniently held with a pair of pincers (preferably with platinum tips) should be dipped in a beaker or other vessel containing concentrated nitric acid (1.42 specific gravity) and immediately afterwards held under an abundant stream of running water. When iron is immersed in concentrated nitric acid it assumes the passive state, that is it is not affected by it. As soon, however, as the layer of concentrated acid which covers the polished surface is diluted by the running water, the steel is vigorously attacked but

for so short a time (since the water soon removes all traces of acid) that there is little danger of etching too deeply. One such treatment is generally sufficient to bring out the structure sharply and clearly, but if the specimen is found insufficiently etched, the etching should be repeated in exactly the same manner. The author believes that the simplicity of this etching treatment and the excellent results generally obtained have been overlooked by metallographists.

Sodium-Picrate Etching of Cementite. — Cementite is not acted upon by the usual reagents employed for the etching of steel sections but remains brilliant and structureless. Kourbatoff, however, discovered a reagent which deeply colors cementite while leaving the ferrite unaffected, thus affording a sure means of distinguishing between the two. The treatment consists in immersing the polished sample in a boiling solution of sodium picrate in an excess of sodium hydroxide for some 5 to 10 minutes, when the cementite assumes a brown to blackish coloration. The etching solution may be prepared by adding 2 parts of picric acid to 98 parts of a solution containing 25 per cent of caustic soda, for instance 2 grams of picric acid in 98 cubic centimeters of a solution made up of 24.5 grams of caustic soda and 73.5 cubic centimeters of water.

Stead's Reagent for the Detection of Phosphorus Segregation in Iron and Steel. — For the detection of phosphorus segregation in iron and steel Stead recommends the following method which he considers superior to his heat-tinting method:

The reagent is made by mixing —

Cupric chloride	10 grams.
Magnesium chloride	40 “
Hydrochloric acid	20 cubic centimeters.
Alcohol to make up to . .	1000 “ “

The salts are dissolved in hot water to saturation and the solution made up to 1000 cubic centimeters with alcohol. Magnesium chloride is not necessary, but better results are, if anything, obtained by having it present.

“The specimens are simply covered with a thin layer of the reagent and must on no account be immersed in a bath of the liquid. The layer of liquid, after remaining on the surface for one minute, is shaken off and a second layer dropped on the surface and left there for the same period. This procedure is repeated as often as it is found desirable. The specimen is washed with boiling water, then with methylated spirits, and shaken to remove the spirit from the surface, the heat imparted by the boiling water rapidly evaporating the last traces of alcohol. The copper is usually left as a hard coherent layer, and is not readily removed by rubbing; indeed, the specimens may sometimes be repolished by rouged chamois leather without disturbing the deposited copper. The reagent not only indicates variations of phosphorus, but by progressive etching one can get a very good idea as to the degree of difference between the phosphorus in different portions of the same metal. If the reagent be applied in successive portions and the difference in the proportion of phosphorus be slight, as stated above, the copper invariably precipitates on the purer portion first; but on repeated application the copper gradually deposits also on the parts richer in phosphorus, and after many applications of the reagent the whole surface, including the phosphorized parts, becomes coated with copper. If, however, the phosphorus be very much concentrated in one or more parts, these remain perfectly bright and free from copper even after ten applications of the reagent.”

Heat-Tinting. — Heat-tinting is described by Stead, its originator, as follows: "Heat-tinting consists in heating polished specimens of metals until their surfaces become colored by oxidation films.

"Alloys of iron and phosphorus, and commercial steel, contain part of their mass richer in phosphorus than other portions. In fact the iron and the phosphide are seldom intimately mixed in ordinary steel. When polished specimens are placed on the surface of a molten bath of tinman's solder,¹ and the heat gradually raised, the portions of the specimens richest in phosphorus assume oxidation tints earlier than the purer parts; hence it follows that by the time the phosphorus-rich parts have passed through the transition stages of yellow-brown, to red and purple, the purer portions will have reached the yellow-brown or red stage, and if at this point the specimen be removed from the source of heat, the phosphorus-rich portions will appear under the microscope as purple or blue on a yellow-brown or red background. If the heating of the specimen be continued, the phosphorized part will assume a yellowish-white tint, while the purer part will reach the blue stage. Each part will pass through the complete range of color from yellow to blue and then to nearly white, but not at the same time, because the purer portions always lag behind, the degree of lag depending on the variation in the proportions of phosphorus in the different parts.

"Heat-tinting is also useful in intensifying the difference in color between ferrous sulphide and manganese sulphide when present together in steel. On heating polished metal containing inclusions of each sulphide until it appears to assume a uniform brown tint, the ferrous sulphide, which is naturally pale yellow, will be found under the microscope to have been colored purple, while the manganese sulphide, naturally a pale dove color, will have become white. If the heating be continued until the surrounding metal becomes blue, the ferrous sulphide will be blue and the manganese sulphide yellow.

"To obtain good results by heat-tinting, it is absolutely necessary first to apply to the surface a very dilute solution of some acid in alcohol. Picric acid answers admirably, but care must be taken to remove the solution employed before it has time to develop the pearlite or sensibly to etch the metal. After thoroughly washing the specimen in water, it is dried with a perfectly clean rag and heated on a hot plate to about 150 deg. C. It is again rubbed with a warm clean cloth, and is then ready for heating to produce the color tint.

"It is difficult to explain why the preliminary acid treatment is necessary, but that it is so is proved in practice, for if it is omitted, the tinting is always unsatisfactory. It is possible that, during polishing, some of the softer metal becomes spread over the harder part, forming an exceedingly thin layer. This, however, is only a surmise."

Sulphur Printing. — The presence of sulphur in steel, especially when segregated, can be sometimes clearly revealed by a laboratory test known as "sulphur printing." As first described by Heyn and Bauer, it consisted in pressing upon the previously polished steel surface strips of silk impregnated with mercuric chloride and hydrochloric acid (10 grams mercuric chloride, 20 cubic centimeters of water, and 100 cubic centimeters of hydrochloric acid). The reaction between the acid and the sulphides wherever present generates H_2S (sulphuretted hydrogen) which in turn reacts with the mercury salt producing stains of mercury sulphide varying in intensity according to the amount of sulphur present in the steel and revealing the spots where the latter occurs.

¹ An iron plate heated by a Bunsen gas burner may be used instead. (Author.)

A better method (Baumann) consists in substituting for the silk ordinary silver bromide (photographic) paper moistened with dilute sulphuric acid, the generated H_2S producing dark stains on the paper where metallic sulphides were present in the steel.

The following more explicit instructions may be followed with good results. The sample to be tested should be filed flat and rubbed on two or three grades of emery-paper, finishing with French paper No. 0. Sheets of Velox printing paper or its equivalent should be soaked until saturated in dilute sulphuric acid (2 per cent solution). The paper should then be placed on a piece of plate glass and the steel specimen, after washing it in clear water, gently pressed upon it for some 20 seconds, when it should be removed and the paper placed in sodium hyposulphite to remove the excess bromide, washed and dried. While theoretically areas containing phosphorus should also darken the bromide paper Stead reports that the staining from this cause is almost imperceptible.

Law covers the steel section with a coating of gelatine containing an acid solution of lead, mercury, or cadmium salt; the acid decomposes the iron or manganese sulphides and the resulting H_2S reacting with the lead or cadmium salt produces brown or yellow stains of lead, mercury, or cadmium sulphide. Rohl writes: "Care should be taken that the gelatine be as thick as possible, so as to be stiff enough to avoid its flowing off or shifting its position after being applied. The gelatine should be applied hot to the slide by means of a glass rod. This method permits of testing under the microscope, for its sulphidic nature, an enclosure placed in the microscope and observed thereon, the stage being screwed back for the purpose of applying the gelatine, so that the place observed by the eye may be at once observed again in the microscope. Weak magnification has been found sufficient and practical for this purpose."

F. Rogers describes a method for taking sulphur prints of *fractures*, consisting in the use of a gelatine emulsion of silver bromide coated upon a very stiff grease clay and soaked in a dilute acid solution containing also a toughening agent. This emulsion is immediately pressed into contact with the clear fracture for a few seconds and withdrawn.

According to Rohl, ferrous sulphide is considerably darkened by one per cent solution of organic acids in ethyl alcohol, after 5 minutes' etching, as compared with manganese sulphide. The same author writes that after a short preliminary etching with alcoholic solutions of organic acids (preferably picric acid), the successive tempering to dark yellow leaves the ferrous sulphide blue and the manganese sulphide a dull whitish. The reaction appears to be well adapted for distinguishing between the sulphides.

Etching Wrought Iron. — The polished samples should be immersed for 10 or 15 seconds in a 10 per cent alcoholic solution of nitric acid or for 30 seconds in a 5 per cent alcoholic solution of picric acid, washed in alcohol and dried with the usual precautions. Concentrated nitric acid may also be used.

The etching treatment should have outlined the joints between the ferrite grains clearly and sharply. If the structure lacks clearness it is safe to infer that the etching was not properly done. In that case the sample should be rubbed a few times on the chamois leather block and again examined without repeating the etching. If the structure remains ill-defined, rub the specimen a minute or two on the rouge block or disk, wash, dry, and repeat the etching treatment until satisfactory results are obtained.

Should the boundaries of the ferrite grains appear too faint, the etching treatment should be repeated without repolishing, so as to etch these lines more deeply.

As the usual purpose of the microscopical examination of samples of wrought iron is to ascertain the quantity and mode of occurrence of the slag and the dimensions of the ferrite grains, it is not generally desired to etch the sample so deeply that some of the grains become deeply colored, still less that etching pits begin to appear.

As an experiment, however, it is advisable to etch samples of wrought iron gradually so that the different stages of the structure may be clearly seen: (1) before etching: slag fibers and a brilliant structureless matrix, (2) after a slight etching: ferrite grains sharply defined but remaining uncolored or but slightly colored, (3) after a deeper etching: some of the ferrite grains deeply colored, and (4) after a still deeper etching: small cubic etching pits beginning to appear.

The production of these etching pits, however, is often a troublesome and uncertain operation. Heyn recommends for that purpose etching with double chloride of copper and ammonium, others (Stead) "a sufficiently long immersion in lukewarm 20 per cent sulphuric acid, followed by cleaning in nitric acid," or again (Le Chatelier) "an acidulated solution of ferric chloride."

Etching Pearlitic Steels. — Pearlitic steels should be etched with the reagents already indicated, namely, nitric acid and alcohol, picric acid and alcohol or concentrated nitric acid, the manipulations being the same as those prescribed for etching wrought iron. An immersion of 10 seconds in nitric acid or of 20 seconds in picric acid generally suffices. The contrast between the bright ferrite or brilliant cementite and the dark areas of pearlite should be very marked. If considerable free ferrite is present its grains should appear like a delicate but distinct network. The absence of this network is generally due to too slight an etching. Under high powers the pearlite should appear distinctly laminated, although it is not always possible to bring out the structure of every particle of that constituent.

Etching Sorbitic Steel. — The etching of sorbitic steel is similar to that of pearlitic steel both in regard to reagents used and manipulations with the exception that sorbite generally etches somewhat more quickly than pearlite. Immersions of 7 or 8 seconds duration in nitric acid or of 15 seconds in picric acid generally suffice. The sorbitic areas will have a granular but ill-defined structure.

Etching Troostitic Steel. — Troostite is etched more quickly and is more intensely colored than any other constituent of steel. For that reason very short immersions are advisable, namely 2 or 3 seconds in nitric acid or 5 seconds in picric acid or better still longer immersions in weaker acids (5 per cent nitric acid or 2 per cent picric acid). Such short etchings do not as a rule bring out the structure of the martensite which generally accompanies troostite, it being left white and structureless. To develop its structure deeper etchings are required.

Etching Martensitic Steel. — Martensite is colored more quickly than pearlite and sorbite but more slowly than troostite, hence the immersions of martensitic samples in the etching baths should be of relatively short duration, 5 seconds in nitric acid or 10 seconds in picric acid. The acicular or zigzag structure of martensite should be brought out, but high power may be needed to resolve it.

Etching Austenitic Steel. — Austenite does not occur in commercially treated carbon steel but may be produced by some drastic treatments as later explained. It also occurs normally in certain alloy steels, as for instance in Hadfield manganese steel. When present in carbon steels its structure may be revealed by short immersions in

nitric or picric acid. It generally remains bright while the martensite often accompanying it is darkly colored. Some writers claim, however, that it may sometimes be colored darker than martensite. In the absence of much martensite its structure is polyhedral. Martensite is readily identified through its acicular or zigzag occurrence. The etching of austenitic alloy steels is dealt with in the following paragraph.

Etching Alloy Steels. — While the reagents and methods used for the etching of ordinary carbon steels are frequently effective for the etching of alloy steels, especially for those which after slow cooling become pearlitic, some of them are refractory to these treatments, much longer immersions being required to bring out their structures while in a few instances the ordinary methods must be deeply modified.

According to some, manganese steels should be etched deeply in picric or nitric acid, washed in water and dried without any attempt at removing the dark colored films covering the surfaces of the specimens.

High speed steel may be etched with nitric or picric acid alcoholic solutions of ordinary strength, but the time needed varies between a few minutes and more than an hour according to the thermal treatment to which the specimens have been subjected, high heating followed by quick cooling generally requiring long immersions. In the author's laboratory, Mr. M. Yatsevitch has developed a very useful method for high speed steel. Ten cubic centimeters of commercial hydrogen peroxide are mixed with 20 cubic centimeters of a 10 per cent solution of sodium hydrate in water. The steel samples are immersed in this solution for 10 to 12 minutes, washed first with water and twice with alcohol and dried, preferably with a blast. The reagent should be prepared fresh every day. After the treatment indicated above the polished samples remain bright and their matrix structureless, but the free carbide containing tungsten is found to have been colored dark. While it is probable that other special carbides such as carbide of molybdenum would be likewise colored, no other constituent appears to be acted upon by this reagent, not even iron carbide (cementite). The method affords a means of bringing out clearly the amount of free carbide in high speed steel and of distinguishing between it and other constituents.

Etching Cast Iron. — The etching of polished samples of cast iron is conducted in every respect like the etching of steel specimens. To bring out clearly the phosphide eutectic and to prevent its being mistaken for pearlite areas or vice versa the heat-tinting method devised by Stead is very useful. Polished samples of gray cast iron should generally be first examined before etching, the distribution, size, and form of the graphite particles being then more clearly revealed.

Etching for Macrostructure. — To reveal the macrostructure, that is the structure visible with the naked eye, and also to detect local segregations, especially of phosphorus, Portevin recommends the immersion of the polished samples for 3 minutes in double chloride of copper and ammonium (10 grams of the double chloride in 120 cubic centimeters of water) followed by an immersion of 30 minutes in 10 per cent nitric acid. Heyn and Stead mentioned immersion of 2 minutes in a 10 per cent solution of cupric ammonium chloride in water, the deposits of copper being removed under a stream of water, while gently rubbing the surface with the fingers or a piece of chamois leather. Similar results are obtained by etching in 20 per cent nitric acid in water, or in dilute hydrochloric or sulphuric acid.

Examination. — The prepared sample should be suspended to the magnetic specimen holder previously described in such a way as to expose to view as much as possible of its surface. The source of light and condensers should be adjusted so

that a beam of light of suitable size enters the vertical illuminator; the light beam should cover a little more than the aperture of the illuminator. A 2-in. (5X) eye-piece and a 16-mm. ($\frac{2}{3}$ -in.) objective will be generally a satisfactory combination for the first examination. The image of the specimen should be focused roughly by the rack and pinion motion of the stage, and the milled head of the vertical illuminator turned tentatively and gently right and left until the sample appears brightly and uniformly lighted. The object should now be brought to a sharp focus by means of the fine adjustment.

As previously stated, if the structure lacks clearness it is safe to infer that the etching was not properly done. In that case the sample should be rubbed a few times on the chamois leather block and again examined without repeating the etching. If the structure remains ill-defined, rub the specimen a minute or two on the rouge block or disk, wash, dry, and repeat the etching treatment until satisfactory results are obtained.

Examinations with high-power objectives (4 mm. or higher) require greater care and more delicate manipulations. It is especially for high-power work that the plain disk illuminator is superior to the prism type.

The specimens should be examined systematically over their entire surfaces, for which purpose a mechanical stage is invaluable, in order to judge of the uniformity or lack of uniformity of its structure. It should be borne in mind that the portions of heat-treated specimens corresponding to the outside of the original samples are very likely to be decidedly lower in carbon owing to the decarbonizing atmosphere generally present in heating furnaces. It is often advisable first to examine the specimens before etching for the presence of slag or other enclosures, graphitic or temper carbon, minute blow holes, etc., these being more readily detected in the unetched condition.

In studying the structure of forged or rolled samples, specimens should generally be prepared corresponding to their cross sections as well as to their longitudinal sections, in order to detect any possible distortion or orientation of structure caused by the forging or rolling.

Photomicrography. — After having selected the spot to be photographed, light-tight connection should be established between the microscope and the camera (in the case of the inverted metalloscope the camera and microscope are permanently connected) and the light carefully adjusted so as to obtain on the screen of the camera as bright and even an illumination as possible. The image should now be focused as sharply as possible, using a focusing cloth if necessary and gently turning the fine adjustment screw of the stand. A focusing glass may be used with great advantage for this operation and is of special importance when photographing with high-power objectives. It should be placed on the plain glass circle which occupies the center of the screen of the camera, and the image focused while being viewed through this lens. By this means we magnify the image formed upon the camera screen, and are therefore able to focus it more sharply in its finer details. Considerable light, however, is lost and the object will often appear but dimly lighted. The rule is to secure the clearest possible image while working tentatively the fine adjustment in both directions, bearing in mind that, at its best, the image may appear blurred and dimly lighted.

An ordinary eye-piece may be used in place of a focusing glass with, in many cases, satisfactory results.

Exposure. — After the image has been properly illuminated and focused the sensitive plate should be introduced and exposed, with the ordinary precautions, for a suitable length of time. The required time of exposure will vary according to (a) the kind of photographic plate used and (b) the amount and nature of light reaching the plate, which in turn will depend upon (1) the nature of the prepared surface, especially its power to reflect light, (2) the kind of illumination used, (3) the position of the diaphragm or diaphragms controlling the amount of light allowed to reach the plate, (4) the kind of light filters used, if any (5) the resolving and magnifying powers of the combination of objective and eye-piece used, and (6) the distance between the screen of the camera and the object.

Specimens which after etching remain quite bright naturally reflect more light and consequently require for their photography a shorter time than duller specimens. Generally speaking the higher the magnification the less light, hence the longer the exposure. The use of colored screens or solutions (light filters) as a rule lengthens the exposure considerably. By placing the screen of the camera at a greater distance from the object (i.e. by extending the bellows of the camera) the magnification is increased but with accompanying loss of light and, therefore, increased length of exposure.

Using a rather slow plate, no screens, a combination of objective and eye-piece yielding a magnification of 100 diameters at a distance of 24 to 30 inches from the object, the diaphragm being wide open, the exposure for most iron and steel samples would vary between a fraction of a second with a powerful arc lamp and some 10 to 20 minutes with a Welsbach lamp. The use of higher magnifications, of screens, and the closing of the diaphragm may lengthen the exposure to such an extent as to require 1 minute or more with an arc lamp and one hour or more with a Welsbach lamp.

The use of sources of light of greater intensity than the Welsbach mantle but less intense than the electric arc, such as the Nernst lamp, the acetylene lamp, or the oxy-hydrogen lamp, calls for exposures of intermediate lengths between the two extremes considered in the preceding paragraph.

When using the photomicrographic apparatus Figure 33, Seed's orthochromatic "L" plates, a special green screen, the illuminator diaphragm being wide open, the shutter diaphragm closed at 7.5, and the distance between the upper lens of the eye-piece and the screen of the camera being 385 mm., the following exposures in seconds for various combinations of objectives and eye-pieces will generally yield excellent results:

EXPOSURE AND MAGNIFICATION TABLE

EYE-PIECES (magnification when used as magnifiers)

		5 ×	6.4 ×	7.5 ×	10 ×	12.5 ×	15 ×
OBJECTIVES (equivalent focal length in millimeters)	32	5 (25)	7 (35)	9 (40)	11 (50)	13 (65)	15 (80)
	16	7 (75)	10 (100)	12 (115)	15 (150)	18 (190)	20 (235)
	4	15 (310)	20 (425)	25 (500)	30 (650)	35 (825)	40 (1000)

EXPOSURE IN SECONDS

Numbers between parentheses indicate approximate magnification in diameters

Diaphragms and Shutters. — It is sometimes advantageous to be able to control the pencil of light entering the illuminator with a view of securing sharper definition. To that effect an iris diaphragm suitably mounted should be placed between the condensing lens or lenses and the vertical illuminator. Some sort of an automatic shutter is convenient to control the exposure of the plates. This shutter may advantageously be combined with the iris diaphragm. Instead of being placed between the source of light and the vertical illuminator, diaphragms and shutters are sometimes inserted between the camera and the microscope. The best disposition consists in placing an iris diaphragm between the condensing lenses and the vertical illuminator, thus controlling the amount of light entering the latter, and another diaphragm combined with automatic shutter between the camera and microscope tube.

Monochromatic Light. — The different sources of light used for microscopical work yield white light and since the correction, even of apochromatic objectives, for chromatic aberration is never perfect, it is evident that the use of monochromatic light, i.e. light of one wave length, is theoretically preferable, especially for photography.

Monochromatic light may be obtained in two ways: (a) by using a source of light actually monochromatic, and (b) by causing white light to pass through colored glass screens or colored solutions (light filters), preventing the passage of some undesirable rays. The mercury arc lamp yields a nearly monochromatic light and has been tried by Le Chatelier with satisfactory results. It seems more convenient, however, when monochromatic light is wanted, to use light filters of suitable colors, in which case colored glass screens will be found easier to manipulate than glass cells containing colored solutions. The author recommends a special green screen supplied by Nachet of Paris or its equivalent.

Photographic Plates. — The use of orthochromatic plates together with a suitable screen is recommended.

Development. — Formula and directions accompany each box of plates, and the student could not do better than to follow them faithfully.

Printing. — Any printing out or developing paper may be used, the printing, developing, or toning being conducted in the usual way. Drying on ferrotype plates affords a quick means of finishing the prints and giving them a satisfactory luster. It is recommended to trim the prints round 2 to $2\frac{1}{2}$ inches in diameter, by means of a margin trimmer and suitable circular forms, as this will give them a very neat appearance.

CHAPTER III

APPARATUS AND MANIPULATIONS (*Continued*)

The apparatus used by the author and his methods have been described in Chapters I and II. Other instruments and manipulations are here briefly mentioned.

POLISHING AND POLISHING MACHINES

Sorby in his pioneer work polished his samples on emery-papers of increasing fineness followed by rubbing with tripoli, crocus, or Water-of-Ayre stone, and finally with jewelers' rouge. Emery-papers are still used, but for quick polishing they are often replaced by emery-powders spread wet on revolving wheels; the author has retained the use of tripoli powder for the treatment preceding the final polishing but others now prefer specially prepared flour-emery or diamantine; jewelers' rouge is still widely used for the final treatment, although some prefer specially prepared alumina, as first suggested by Le Chatelier.

In 1904 Osmond's polishing method consisted in roughing off with emery and polishing with rouge. Emery-papers of increasing fineness were stretched over glass plates. The papers used were prepared by mixing with water levigated "120 minutes" emery¹ and collecting the deposits formed at the end of increasing periods of time in precipitating glasses. The classified powders, after drying, were mixed with a mucilage of albumen (made up of 72 cubic centimeters of albumen and 28 cubic centimeters of water beaten to a froth and, after 12 hours, strained through a fine-meshed sponge) and spread on paper of the best quality. Osmond also prepared his own rouge by calcining copperas at as low a temperature as possible and separating the finest product by levigation. The rouge was spread on a piece of cloth stretched over the cast-iron table of a small horizontal polishing machine and used wet.

In 1900 Le Chatelier's method of polishing specimens of iron and steel previously rubbed upon emery-papers, including the finest grades, consisted in rubbing them successively (1) on emery-paper prepared with albumen, according to Osmond, with the deposit obtained in between a quarter of an hour and one hour in the ammoniacal washing of flour-emery, (2) on a felt disk covered with some soap paste prepared with the deposit of alumina or of emery, obtained in between one and three hours, (3) on a flat disk made of wood, metal, or ebonite, covered with cloth, velvet, or leather strongly glued upon it; upon this covering the soap preparation, obtained with the deposit of alumina after twenty-four hours, was spread. The last two disks were rotated by some mechanical devices producing great speed. All disks must be frequently moistened with a brush or sponge.

¹ By "120 minutes" emery is meant emery which has taken 120 minutes to settle in a vessel of water of certain dimensions.

According to Gørens, Le Chatelier's method in 1908 consisted in the use of (1) small sheets of French emery-paper, Hubert grades IG and 00 on ground glass plates, (2) flannel stretched over glass covered with "one minute" emery previously passed through a fine sieve (1200 meshes per sq. cm.), some soap solution being also poured over the cloth, (3) a similar support covered with "120 minutes" emery previously passed through a very fine sieve (2600 meshes per sq. cm.) and washed, and (4) a vertically revolving brass disk covered with flannel and washed alumina. The fine alumina mixed with water and soap solution may be sprayed on the disk by means of the sprayer shown in Figure 46.

The preparation of fine alumina powder for the final polishing of iron and steel samples was first described by Le Chatelier in 1900. The method used is that em-

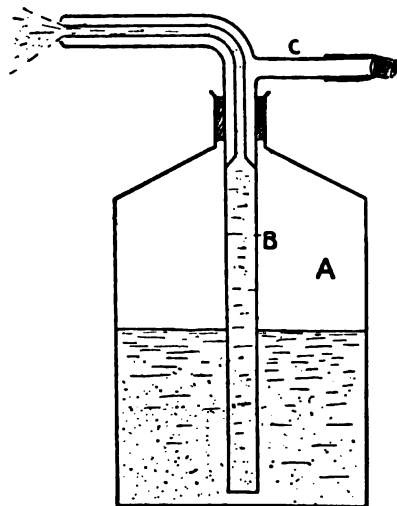


Fig. 46. — Sprayer for emulsified alumina. (Gørens.)

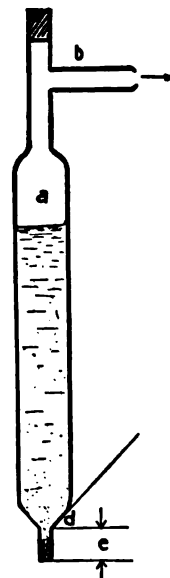


Fig. 47. — Pipette for the levigation of alumina. (Gørens.)

ployed by Schloesing for the analysis of kaolins. The following description of Le Chatelier's manipulation is from Gørens (1908).

The purest precipitated alumina, from ammonia alum, is passed through a sieve, of 2600 meshes per sq. cm., and 100 grains of it in 300 c. c. of distilled water are triturated in a mill for three hours. The whole is then poured into a liter flask, well shaken, and about 200 c. c. pipetted off into a flask closed with a rubber stopper. To this are added 1800 c. c. of distilled water and 2 c. c. of concentrated nitric acid (1.4 sp. gr.), the mixture well shaken, and allowed to settle; the settling is complete in a short time (about two hours). The clear supernatant liquid is siphoned off with an S-shaped siphon; with careful manipulation this is possible to the extent of $\frac{1}{10}$ of the total amount. The liquid drawn off is replaced by distilled water, the mixture well shaken several times, and allowed to settle again, after which the wash water is again drawn off as before. This is repeated three or four times more. At last the supernatant liquid remains milky for a whole day, which is an indication of the per-

fect removal of acid. Finally, distilled water is added for the last time up to about 2 liters, the mixture thoroughly shaken, and the alumina separated from the liquid in the apparatus shown in Figure 47. A pipette *a* of about 500 c. c. capacity is drawn out below to an opening of about 3 mm. internal diameter. The alumina is prevented from clinging by giving an inclination of at least $\frac{1}{3}$ to the sloping sides of the tube. The piece *b* is connected to the water pump. The end (of the pipette) is dipped into the vessel containing the emulsified alumina and the pipette sucked full, whereupon the opening *b* is closed with a screw cap so far that one drop runs out about every fifteen seconds. The material obtained during the first quarter of an hour is very heterogeneous and still scratches the surface of the section markedly, so that it cannot be used. After a quarter of an hour has expired the tap is closed and the alumina allowed to settle completely. After three hours the material is placed in the flask *A* (Fig. 46) provided with a spraying arrangement. Soap solution¹ is added and the mixture diluted with distilled water. The material thus prepared is ready for use, and is suitable for steel and pig iron. The residue which settles in 3 to 24 hours is treated similarly, and serves for polishing softer materials (iron, copper, etc.). The portion which still remains in suspension after 24 hours is too fine and is poured away.

The same method has been applied to commercial flour-emery, oxide of chromium, and oxide of iron, but the resulting products are far from being as satisfactory as the alumina powders.

Revillon has recently described a rapid method of preparing alumina suitable for polishing. A certain amount of alumina is suspended in a large volume of water, well shaken, and allowed to stand for five minutes. The liquid is then siphoned off and with the particles of alumina still held in suspension may be used for polishing. To obtain finer powders 15 to 20 grams of finely ground alumina should be mixed with one liter of distilled water, shaken, and allowed to settle five minutes. Most of the liquid is then siphoned off, transferred into another vessel, and allowed to stand fifteen minutes; the decantation is repeated, etc., a clearer liquid, that is one holding finer particles in suspension, being obtained every fifteen minutes. The final liquid, from which no powder is deposited, may be used for the finest polishing, the intermediate products for rougher work.

Robin has described the preparation of alumina powder by a method based upon the catalytic action of mercury in causing the oxidation of pure aluminum. Strips of aluminum are immersed in mercury for a short time and then exposed to moist air when the small amount of mercury they have absorbed causes the oxidation of the metal, growth of Al_2O_3 taking place, the increase of which is visible with the naked eye. This alumina can be readily detached and as a fine powder may be used for polishing. Robin claimed for his method the advantages of greater simplicity and lower cost.

In 1900 Stead recommended for polishing iron and steel samples the use of emery-papers, Hubert grades Nos. 0, 00, and 000, followed by rubbing with one grain of diamantine powder² spread wet over a smooth black cloth and, for final treatment, gold rouge used dry on chamois leather or, for finer structures, wet on parchment or kid leather. He used a simple, hand polishing machine in which one block at a time was made to rotate horizontally (Fig. 48).

¹ The soap solution is prepared by dissolving pure (Venetian) soap in hot water and filtering through a filter paper into a flask. After cooling the solution should be sirupy.

² Diamantine powder consists of pure alumina and is used by jewelers for polishing steel.

More recently he has described as follows his polishing manipulation: "The surfaces are made smooth by filing or grinding on coarse emery-cloth, and afterwards on progressively finer emery-paper, until the finest French paper 000 is reached.

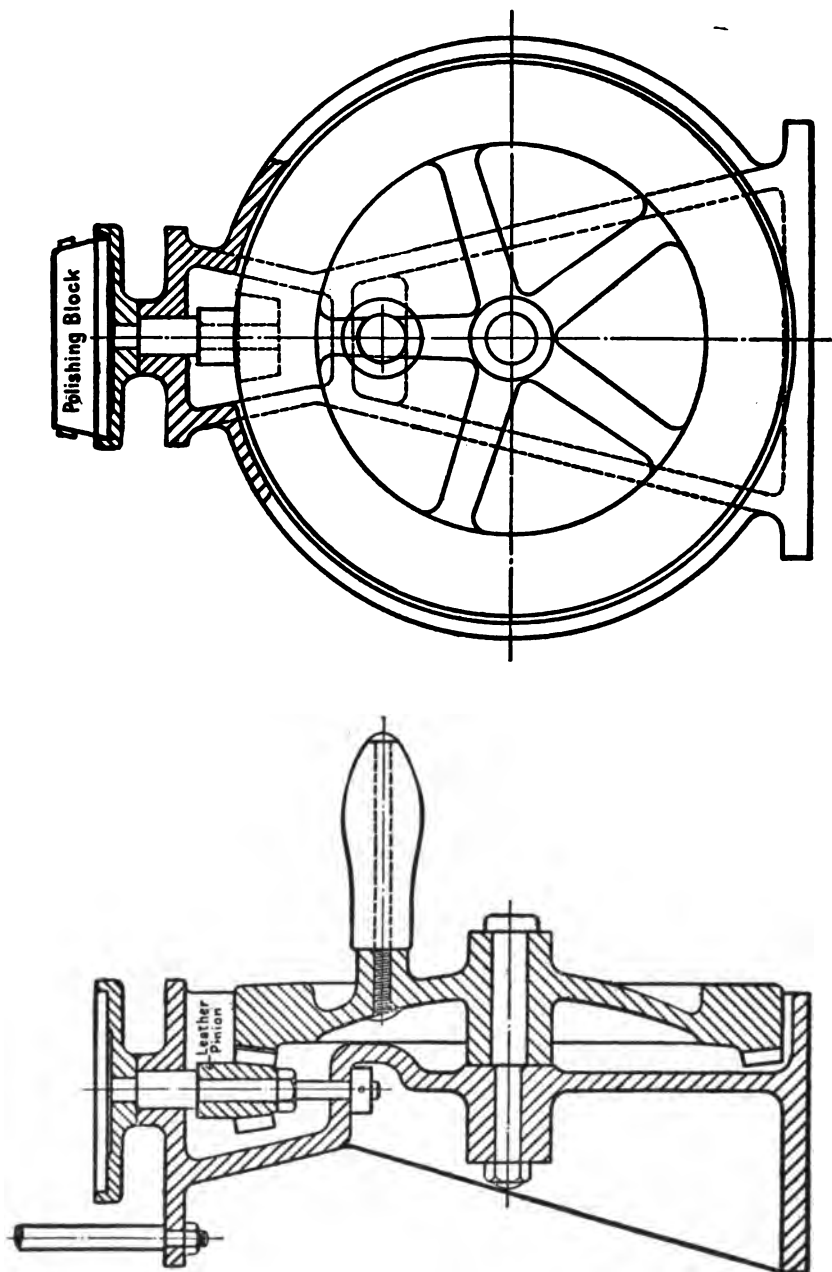


Fig. 48. — Hand polishing machine. (Stead.)

Fine polishing is then conducted on a wheel either having horizontal or vertical motion, and covered with two layers of thick khaki cloth between which a layer of diamantine powder or other specially prepared polishing powder is placed." Water is

run on the prepared surface of the polishing block the speed of which should be at least 1000 revolutions per minute. "Pressure must be applied strongly at first, and then be gradually reduced until finally little more than the weight of the specimen and the fingers pressing it press on the polishing surface. With practice a specimen can be prepared in 10 minutes."

A foot polishing machine also designed by Stead is shown in Figure 49¹ and a larger one to be run by power in Figure 50. In these machines brass disks carrying



Fig. 49. — Foot power polishing machine.
(Stead.)



Fig. 50. — Multiple polishing machine. (Stead.)

conical wooden blocks are attached to vertical spindles and driven from below. Emery-papers are fastened to some of these blocks by means of brass rings slipping over them while others are covered with cloth in a similar way.

The block for fine polishing is covered with a double layer of cloth between which is placed specially prepared calcined alumina in fine powder. Jewelers' diamantine powder answers admirably. Fine polishing is always done on cloth-covered blocks, kept continually moist with clean water. Only the finest parts of the powders find

¹ A similar machine is supplied with electric motor attached.

their way through the porous cloth. Clamps are provided for holding the samples against the revolving disks. The central vessel contains the water needed for wet polishing, a small tap projecting over each disk. The excess water is caught by brass water guards and discharged into a trough below the level of the disks. These machines are made by Carling and Sons of Middlesbrough, England.



Fig. 51. — Foot power polishing machine. (P. F. Dujardin and Co.)

Martens, according to Gøerens (1908), used vertically rotating disks upon which were pasted emery-papers, Hubert brand, grades 3, 2, 1G, 1M, 1F, 0, and 00 and, for final treatment, levigated jewelers' rouge on cloth. The disks made 400 revolutions per minute. The average time needed to polish a specimen varied between $1\frac{1}{2}$ and 2 hours.

Gulliver (1908) recommends for polishing the use of emery-papers grades No. 1,

0, and 00 on hard wood or plate glass and for final treatment the finest rouge or diamantine powder on cloth stretched over hard wood.

The polishing machines shown in Figures 51 and 52 are made by P. F. Dujardin of Düsseldorf. It will be noted that one side only of the disks is utilized. A machine



Fig. 52. — Polishing motor. (P. F. Dujardin and Co.)

like the one of Figure 52 is also made for belt driving. A similar machine is supplied by Pellin of Paris.

Sexton describes the polishing machine Figure 53 made by Baird and Tatlock. Its construction is obvious.

A simple polishing machine consisting of an horizontally revolving disk (Fig. 54) was described in 1899 by Ewing and Rosenhain. *A* is the spindle of an electric motor carrying a small driving disk *B*, fitted with a rubber ring to increase the driving fric-

tion. The polishing disk *C* has a vertical axis running in a bearing on the casting *D*. The under side of the polishing disk bears upon the driving wheel *B* and takes motion from it.

A. Kingsbury in 1910 describes his polishing method. He prepares his supporting blocks by pouring paraffin on brass disks. After solidifying these paraffin blocks which are about $\frac{1}{2}$ inch thick and 8 inches in diameter have their upper face dressed flat. They are made to rotate horizontally in a suitable machine and upon them emery of increasing fineness and finally rouge are used in succession. The speed of the polishing machine is 200 revolutions per minute. The time needed to polish a sample of ordinary steel is given as 15 minutes.

C. Campbell in 1902 described his polishing operation as consisting in rubbing the sample, previously filed smooth, successively on emery-cloth, grades 0 and 00, and on



Fig. 53. — Polishing machine. (Baird and Tatlock.)

French emery-papers, grades 0, 00, 000, and 0000. The specimen is then polished on broadcloth or chamois leather with well washed rouge and water. Some workers, the writer says, use an intermediate stage with diamantine powder.

C. H. Risdale in 1899 described his polishing operation as consisting in (1) rough filing, (2) fine filing, (3) rubbing with rough commercial emery-cloth stretched on a board, (4) rubbing with fine emery-cloth stretched on a board, (5) rubbing on fine specially prepared paper on disks of Stead's polishing machine, (6) rubbing on diamantine on cloth stretched on disks of Stead's machine, (7) rubbing on rouge on washed leather similarly mounted or, for very fine work, on rouge on wetted parchment.

Guillet in 1907 recommended for polishing two carborundum wheels and two suitably selected emery-papers and, for final treatment, alumina on cloth stretched over a revolving disk. He places smooth sheets of zinc between the wooden disks of his polishing machines and the polishing cloths.

In 1901 Arnold described as follows a quick polishing and etching method: "Take two pieces of hard wood, $12'' \times 9'' \times 1''$, planed dead smooth on one side; then by means of liquid glue evenly attach to the smooth faces two sheets of the London Emery Works Co.'s atlas cloth No. 0. Allow the glue to set under strong pressure.

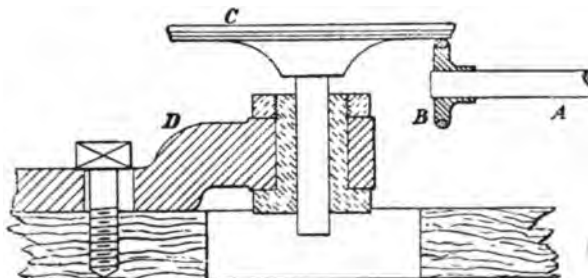


Fig. 54. — Polishing machine. (Ewing and Rosenhain.)

Next, by means of a smooth piece of steel, rub off from one of the blocks as much as possible of the detachable emery. This is No. 2 block, the other, necessarily, No. 1 block.

"The steel section, say $\frac{7}{8}$ inch thick and $\frac{1}{2}$ inch diameter, is rubbed for 1 minute on No. 1 block, the motion being straight and not circular; then, for the same time



Fig. 55. — Polishing machine. (Wysor.)

and in the same manner rub on No. 2 block. Next place the bright but visibly scratched sections in a glass etching dish $3'' \times 1'' \times \frac{1}{2}''$, and cover the steel with nitric acid sp. gr. 1.20.

"Watch closely until in a few seconds the evolved gases adhering to the section change from pale to deep brown and effervescence ensues. Then, under the tap,

quickly wash away the acid and for a minute immerse the piece in a second dish containing rectified methylated spirits. Dry the section by pressing it several times on a soft folded linen handkerchief, when it will be ready for examination. The struc-

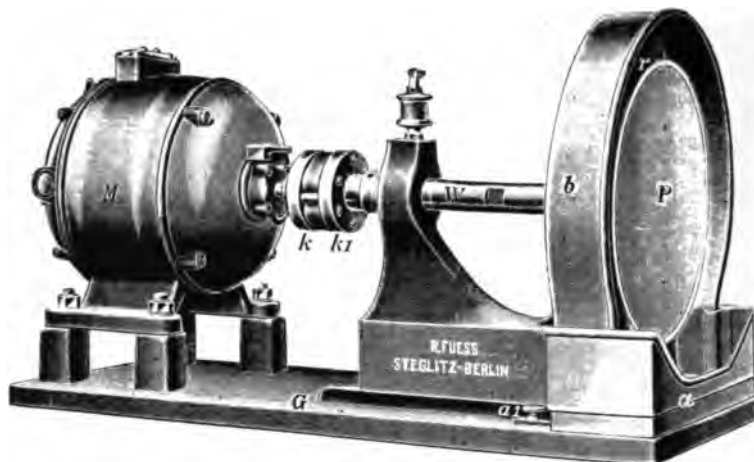


Fig. 56. — Polishing machine. (R. Fuess.)

ture will be clearly exhibited, the innumerable fine scratches visible before etching having virtually vanished."

Robin polishes his samples (1) on carborundum or hard emery-wheel (500 to 1000 revolutions per minute), (2) on fine emery-wheel (1000 revolutions), (3) by hand on

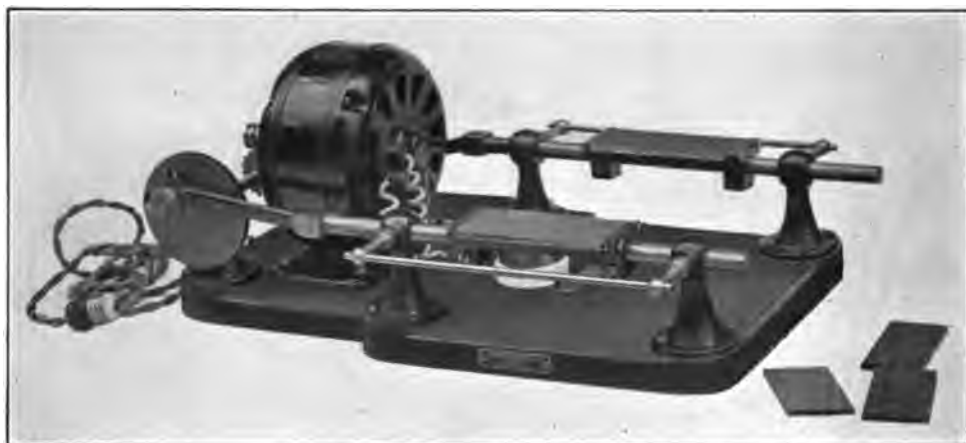


Fig. 57. — Polishing machine. (Scientific Materials Co.)

emery-papers of increasing fineness, and (4) with jewelers' rouge and water on wooden disk (1000 revolutions).

Professor Wysor has designed the polishing machine shown in Figure 55 in which three polishing blocks are made to revolve simultaneously, two vertically and one horizontally.

R. Fuess of Steglitz bei Berlin offers the polishing motor (Fig. 56), in which but one polishing disk revolves at a time.

The Scientific Materials Company of Pittsburg, Pennsylvania, construct the machine illustrated in Figure 57. The motion is reciprocating.

Polishing Small Specimens. — To make possible the polishing of very small specimens or for preventing the rounding of the edges of samples of moderate size, Le Grix uses small brass cylinders which he fills with gum lac and in which he presses the pieces to be polished (chips, cuttings, etc.). The whole is then polished as if it were a solid piece. The modus operandi is as follows: The brass mounting is heated in a Bunsen burner and filled with gum lac used in the form of sticks like sealing wax. After cooling the excess gum is removed with a file to a level with the mount and the specimens pressed into the filling material by means of a preheated metallic blade. When the specimens are very small the polishing operation is very short indeed (Le Chatelier mentions 3 minutes). The etching reagent may be applied to the metallic particles by means of a glass rod thereby preventing the brass mounting and even the gum from coming in contact with it which is desirable since alcoholic solution would dissolve the latter. The same material may also be used with advantage for filling up small cavities such as blow holes occasionally present in samples to be polished, thereby preventing the rounding of their edges or the tearing of the polishing cloths.

DEVELOPMENT OF THE STRUCTURES

The methods which, in common with many workers, the author has found most satisfactory for revealing the structure of polished iron and steel specimens have been described in Chapter II. Other methods have been used that should be mentioned.

Polishing in Relief. — So-called relief polishing has been used successfully by Sorby, Martens, Behrens, and especially by Osmond. It consists in rubbing the specimen on a soft, yielding support with some suitable polishing powder, the softest constituents being, so to speak, dug out, leaving the harder ones standing in relief. These differences of level make it possible to distinguish the constituents under the microscope without further treatment. It is evident that only those samples which are made up of constituents differing much in hardness can be so treated. The free cementite of hyper-eutectoid steel or of white cast iron, for instance, can be made to stand strongly in relief because it is so much harder than the accompanying pearlite or other constituents.

Osmond polished his samples on a damp piece of parchment stretched over a piece of well-planed wood, and rouge was rubbed strongly on the parchment. The block was then put under the tap and washed so that only those particles of rouge that had found their way into the pores of the parchment were retained. To distinguish between raised portions and cavities the luminous rays are strongly diaphragmed and the objective placed a little below the focusing point, is slowly raised. The reliefs, which at first appear brilliant and yellowish on a relatively darker ground, gradually become dark on a bright ground; the cavities present inverse appearances so perfectly that two photographs of the same preparation, taken one a little below and the other a little above the mean focusing point, are almost positive and negative to one another.

Polish-Attack. — For many years Osmond obtained his best preparations by a combined polishing and etching method (*polissage-attaque*) consisting in rubbing the polished sample upon a piece of parchment covered with some aqueous extract of liquorice root, with the addition of precipitated calcium sulphate. In 1899 Osmond and Cartaud recommended replacing the extract of liquorice by a diluted solution of nitrate of ammonium (2 parts by weight of the crystallized salt to 100 parts of water). A piece of parchment spread tightly over a smooth board is soaked with the solution and the specimen rubbed upon it until sufficiently etched. It is not necessary to add any sulphate of calcium.

Etching. — Sorby etched his specimens with very dilute solutions of nitric acid in water and this reagent was widely used for many years by other metallographists. The water has now been replaced by absolute alcohol (Chapter II). Le Chatelier has mentioned the use of glycerine as a satisfactory non-oxidizing vehicle for nitric as well as for picric and hydrochloric acid.

Osmond, the author believes, was the first to use tincture of iodine. This tincture is applied in the proportion of one drop per square centimeter of surface and allowed to act until it is decolorized, the treatment being repeated after examination if needed. Le Chatelier recommends applying the tincture with the tip of the finger and gently rubbing the specimen.

Stead uses a solution made up of 1.25 grains of iodine, 1.25 grains of iodide of potassium, 1.25 grains of water and alcohol to make up 100 c. c. After the iodine has lost its color the sample should be washed in water, then in alcohol, and finally dried in a blast of hot air.

Martens and Heyn in 1904 recommended the use (1) of an etching solution containing 1 part of hydrochloric acid (1.19 sp. gr.) and 100 parts of absolute alcohol and (2) of 1 part of hydrochloric acid in 500 parts of water with the assistance of the electric current.

Heyn used a solution of double chloride of copper and ammonium containing 12 grains of the salt and 100 grains of distilled water.

To distinguish with certainty between iron phosphide and cementite, Matwieff recommends *neutral* sodium picrate washed several times with distilled water to eliminate the excess of picric acid or of sodium that might be present. The sample is immersed in the boiling solution for 20 minutes, a treatment by which the iron phosphide is strongly attacked while the cementite and pearlite remain unaffected.

For etching austenite and martensite Robin recommends the use of a saturated solution of picric acid in alcohol, an immersion of 30 seconds to 1 minute, washing with water without touching the specimen and drying by air blast or simply in air. Films of various tints are formed, ferrite remaining uncolored.

Le Chatelier has used bitartrate of potassium as an etching reagent. It leaves cementite and pearlite uncolored, while it imparts a dirty coloration to ferrite.

The same author has described the use of a freshly prepared reagent made up of equal parts of a solution containing 50 per cent of soda and of a solution containing 10 per cent of lead nitrate. Cementite is quickly colored by it while the phosphides and especially the silicides are also attacked. The reagent is recommended for highly carburized metals. Medium high carbon steels of great purity are not affected by this solution, but when impure, the pearlite is energetically acted upon, probably because of the presence of impurity in that constituent.

Le Chatelier has also mentioned the use of a solution of 10 per cent gaseous hydrochloric acid in absolute alcohol to which is added 5 per cent of cupric chloride for annealed steels and 1 per cent of the same salt for hardened steels. Ferrite and cementite are not colored, martensite very little, austenite a little more, troostite and sorbite decidedly.

The etching reagents usually applied to bring out the structure of unhardened steel, namely, picric acid, nitric acid, tincture of iodine, etc., do not always yield satisfactory results in the case of hardened steel. Kourbatoff discovered a complex reagent which often produces greater contrasts between the various constituents. It is made up by mixing 1 part of amyl alcohol, 1 part of ethyl alcohol, 1 part of methyl alcohol, and 1 part of a 4 per cent solution of nitric acid in acetic anhydride and should be prepared just before use.

Heyn recommends for etching hardened steel a solution containing 1 part of hydrochloric acid and 99 parts of absolute alcohol. More uniform results are obtained if a weak current of electricity be passed through the solution, the samples to be etched forming the positive pole while the negative electrode may consist conveniently of a piece of sheet lead. With the assistance of the electric current the use of a very dilute aqueous solution is advisable, namely, 1 part of hydrochloric acid in 500 parts of distilled water.

Osmond, likewise, used successfully a solution of 10 per cent of hydrochloric acid in water by which the martensite is colored darker than austenite, the treatment requiring several minutes. Osmond writes: "There is more regularity obtained by having the specimen connected, by means of a platinum wire, with the positive pole of a bi-chromate cell, a strip of platinum placed in the acid being connected with the negative pole. In this way the specimen becomes the anode, and the platinum the cathode."

Benedicks recommends for the etching of martensite-austenitic steel a 5 per cent alcoholic solution of metanitrobenzol-sulphonic acid which always darkens martensite more than austenite. Immersions of some 15 seconds are generally sufficient.

Hilpert and Colver-Glauert have described the use of sulphurous acid for non-pearlitic steels and for pig iron. A saturated solution of sulphur dioxide in water is prepared and 3 or 4 per cent of that solution in water used. The time of etching varies between 7 seconds and 1 minute. Alcohol may be substituted for water in which case the etching lasts several minutes. The treatment causes the deposition of layers of iron sulphide of different thickness and, therefore, of different colors, on the various constituents.

Rosenhain and Haughton report interesting results obtained with a solution made up as follows:

Ferric chloride 30 grams, hydrochloric acid (conc.) 100 cubic centimeters, cupric chloride 1.0 gram, stannic chloride 0.5 gram, water 1 liter.

The polished specimen which should be absolutely clean is immersed in the solution for 10 seconds to 2 minutes according to the character of the metal. The action of the reagent consists in the deposition on the surface of the steel of thin films of metallic copper which vary in thickness and therefore in appearance with the various constituents present, producing an effect not unlike that obtained with heat tinting. The authors write that "in practically pure carbon steels the new reagent yields a pattern which is the reverse of that obtained with the ordinary etching reagents, such as picric acid, ferrite being darkened while pearlite remains white; on hardened

steels, especially those of low and moderate carbon contents, the reagent yields very clear results particularly in the etching of martensite, although in this case the patterns are not reversed as compared with those obtained with picric acid, sulphur dioxide, etc. The principal interest and importance of the new reagent, however, lies in the fact that it reveals in a clear and striking manner the distribution of phosphorus, particularly in mild steels."

Howe, according to O. F. Hudson, uses in his laboratory Heyn's reagent (10 per cent copper ammonium chloride in water) for low carbon iron and steel. He finds that it "shows grain boundaries readily, rather obscures Neumann lines" and that it is the best reagent for etching figures and pits. Hoyt uses a similar solution "principally for microscopic examination of low carbon steel, wrought iron, white cast iron, and in the determination of phosphorus segregation in wrought iron."

Electrolytic Etching. — Le Chatelier was one of the first to advocate the use of the electric current in order to obtain a more uniform action in etching iron and steel samples. Sheet lead may be used for the positive electrode and, as electrolyte, a 10 per cent solution of chloride or sulphate of ammonium gives good results. The current needed varies between 0.001 and 0.01 amperes per square centimeter.

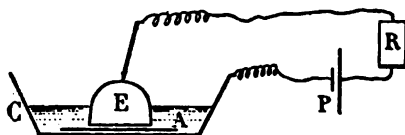


Fig. 58. — Arrangement for electrolytic etching.

Electrolytic etching has been described by Cavalier (1909). A few cubic centimeters of the electrolyte are placed in a platinum dish *C* (Fig. 58) connected with one pole of the battery *P*; the specimen *E* connected with the other pole is placed in the solution, a piece of filter paper *A* being inserted between the dish and the polished surface of the specimen. The current is regulated through the rheostat *R*. Four or five volts are required with an intensity of 0.001 to 0.01 amperes per square centimeter. The attack lasts from a few seconds to a few minutes.

Hot Etching. — Steel while at a high temperature (red heat) has been etched (1) by Saniter in molten calcium chloride heated to the desired temperature, and (2) by Baykoff in a current of gaseous hydrochloric acid.

Washing and Drying. — After removing the specimens from the etching bath, the author washes them in alcohol and dries them in an air blast. Washing in water, in caustic potash, in lime water, and in ether has also been recommended as well as the use of fine linen cloth and of a hot blast for drying.

Preserving. — The author preserves his etched specimens in desiccators and in air-tight cabinets.

Several protective coatings have been described. Stead covers them with paraffin wax dissolved in benzole, which is removed by wiping with a clean linen rag moistened with benzole, when it is desired to examine the specimens. Le Chatelier applies a coating of "zapon," a solution of gun cotton in amyl acetate sufficiently transparent to allow examination with the highest powers.

MOUNTING AND MOUNTING DEVICES

The author's special holders for placing the prepared samples on the stage of the microscope have been described in Chapter I. Other methods have been used and are still employed by some workers, namely, (1) mounting in some plastic material and (2) the use of leveling stages.

Plastic Mounting. — Osmond mounted his specimens by embedding them in a little soft wax placed upon a glass plate. The leveling is managed by means of two pieces of glass tube of equal height, one on each side of the sample.

Stead places the specimens polished face down on a piece of plate glass (Fig. 59) and surrounds them with brass cylinders accurately turned. A piece of plastic wax is stuck upon the center of a glass microscope slide and is then pressed upon the sec-

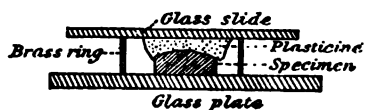


Fig. 59. — Stead's mounting device.
(C. H. Desch's Metallography.)

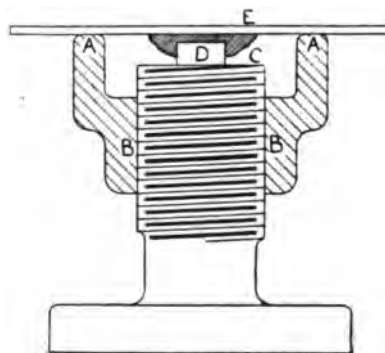


Fig. 60. — Gulliver's mounting device.

tion till the glass slide comes in contact with the brass ring. The specimen adheres to the wax and the mounting is complete.

Gulliver (1908) describes the device (Fig. 60) for mounting specimens. It consists of a circular ring faced on its upper surface *A*, and screwed internally at *B* to fit the foot, of which the upper end *C* is also faced. The distance between the parallel faces *A* and *C* can thus be adjusted. The specimen is placed at *D* and a glass slide *E* with some soft modeling clay or wax is pressed upon it until the glass touches the ring at *AA*.

Mechanical mounting devices working on the principle of the microtome have also been used. They have been described by M. A. Richards: "Projecting from a cylindrical metal base three inches in diameter, is a threaded upright three and one-half inches in diameter. A cylindrical nut or collar three inches high and two and one-half inches outside diameter screws on the threaded upright. A small circle of chamois skin is placed on the top of the threaded upright to protect the etched face of the micro-section. To mount a section, place it face down on the chamois skin, press upon the upper projecting portion a lump of beeswax, and upon this place the ground glass (ground surface down). A few revolutions of the collar will cause the glass to rest upon the upper edge of the collar, and the adhesion of the glass and beeswax to the specimen may be made complete by slowly turning the collar down with one hand

while keeping the glass base in close contact with the collar-top with the other hand. In this manner, no matter how irregular the section, the parallelism of the etched surface and the glass base may be very quickly and accurately obtained."

The mounting device (Fig. 61) is constructed by Watson and Sons. It consists of two horizontal plates, the upper one being capable of vertical movement but always



Fig. 61. — Watson and Sons' mounting device.



Fig. 62. — Watson and Sons' leveling stage.

remaining parallel to the lower one. The specimen is placed with its polished surface on the lower plate, and the upper plate carrying a glass slip to which some suitable clay or wax is attached is lowered into contact.

Leveling Stages. — The leveling stage (Fig. 62) is one of several constructed by Watson and Sons, London. The specimen is held by two rotating jaws and can be leveled by means of the screws *A* and *B*.

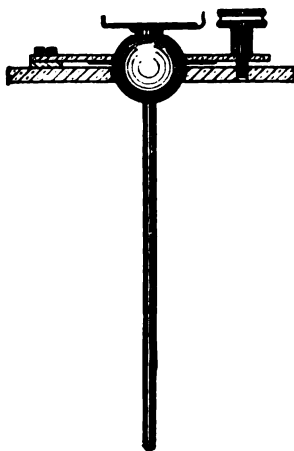


Fig. 63. — Huntington's leveling stage.

Professor A. K. Huntington devised the leveling stage shown in Figure 63. It is provided with a ball and socket joint for leveling, permitting the placing of the sample in any position.

Other forms of leveling stages are shown in some of the illustrations in the following pages as part of some metallurgical microscopes.

METALLURGICAL MICROSCOPES

The microscopes and accessories used by the author have been fully described. In the following pages instruments used by some other workers or described by them, as well as those manufactured by well-known makers, are mentioned.



Fig. 64. — Le Chatelier's inverted metallurgical microscope.
Early form.

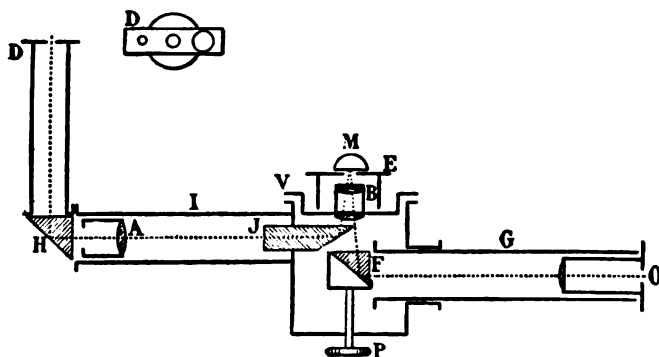


Fig. 65. — Le Chatelier's inverted metallurgical microscope.

Le Chatelier. — In 1897 Le Chatelier devised an inverted microscope which later he greatly improved and which is now constructed with unimportant modifications by several microscope makers. An early form of Le Chatelier's instrument is shown in Figure 64 and its more recent construction in Figures 65 and 66. The objective

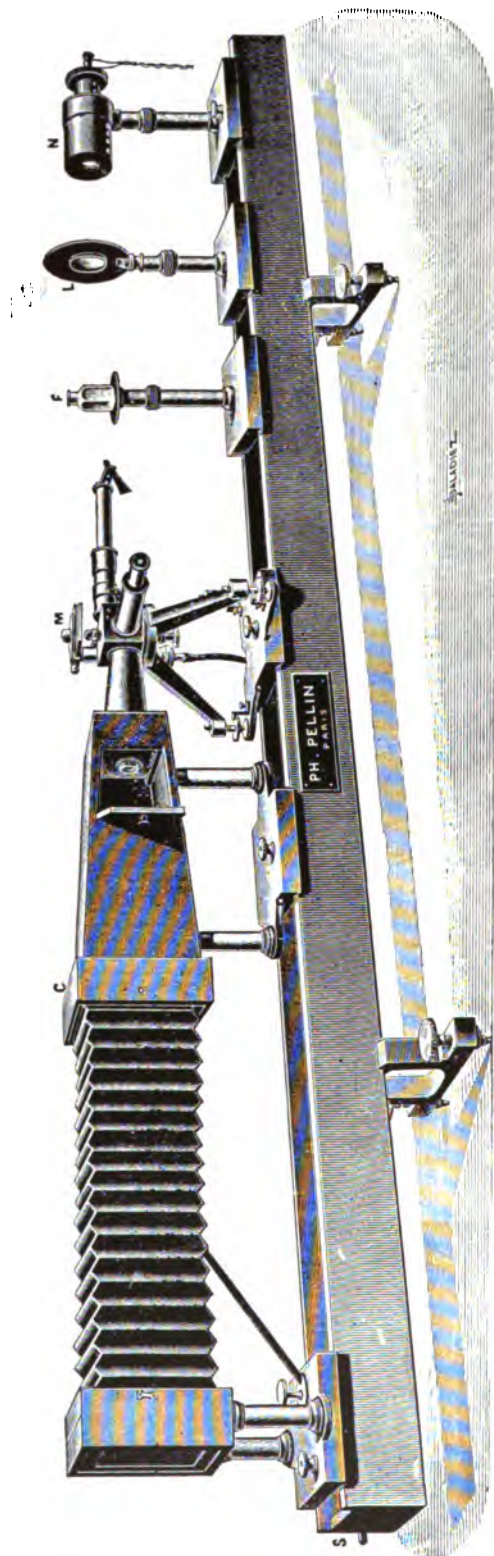


Fig. 66. — Le Chatelier's inverted metallurgical microscope.

B (Fig. 65) is directed upwards while the eye-piece *O*, placed horizontally, receives the image by the reflection of a totally reflecting prism *F* placed below the objective. The prism *F* may be rotated by means of the milled head *P* and the light reflected by the objective turned at will into the tube *G* and the eye-piece *O* for visual examination

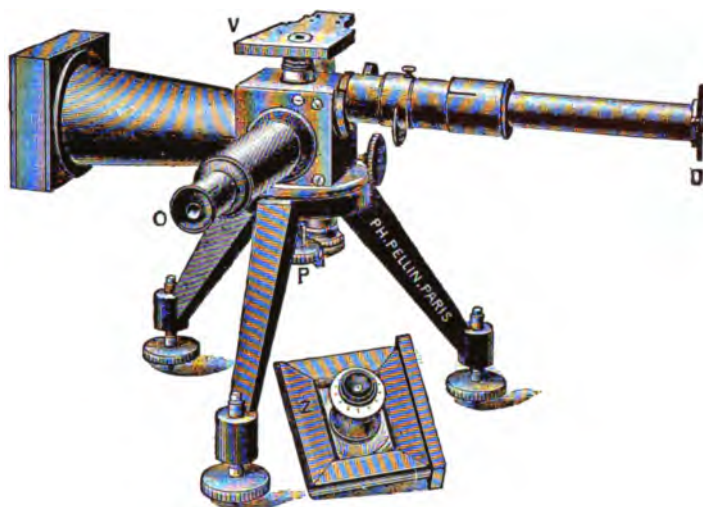


Fig. 67. — Le Chatelier's inverted metallurgical microscope.

or into another tube connected with a camera for photographing (Fig. 66). The light is condensed by the lens *A* and, being deflected at right angles by the prism *J*, passes through the objective *B* and reaches the object *M* placed on the stage *E*. In

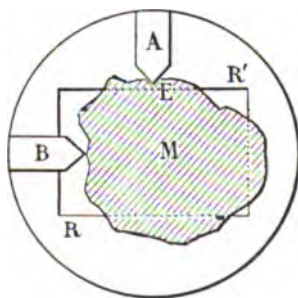


Fig. 68. — Device for placing specimens on the stage of the Le Chatelier microscope in a fixed position. (Le Grix.)

case the light is placed at a higher level than the condensing lens *A*, it must be received by a totally reflecting prism *H* which directs it into the condenser *A*. *D* is a diaphragm placed at the principal focus of the complex optical system composed of the objective *B*, the illuminating prism *J*, and the lens *A*. The opening as well as the

position of the diaphragm may be altered. Another diaphragm placed at *I* affords a means of stopping the light which would fall upon parts of the preparation outside of the portion examined and which would increase the blur resulting from the reflection of useless rays by the back lenses of the objective. In the early construction of

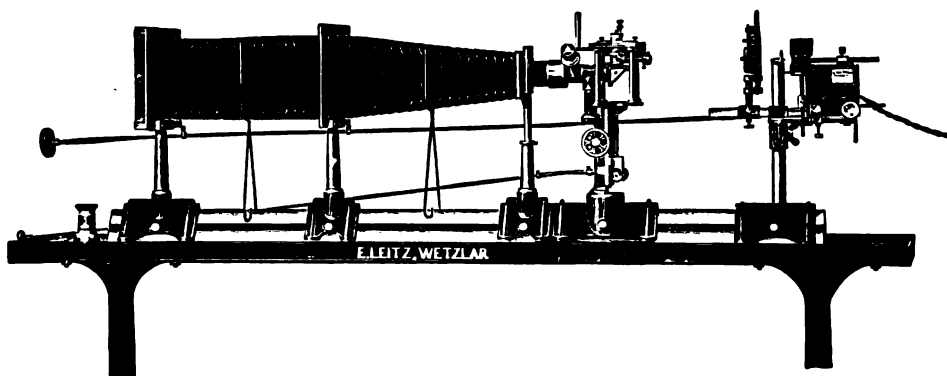


Fig. 69. — Inverted metallurgical microscope constructed by E. Leitz.

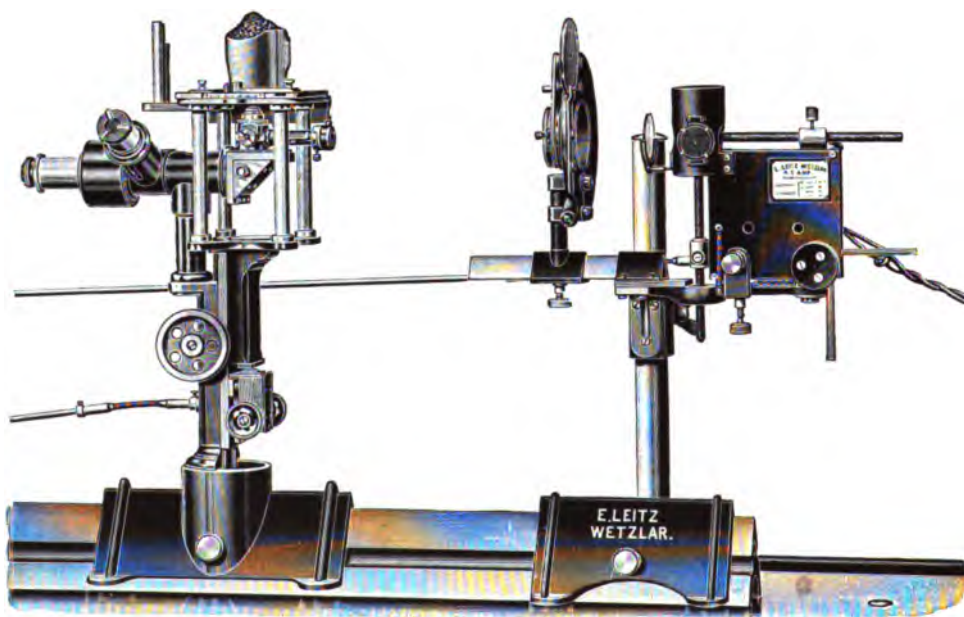


Fig. 70. — Inverted metallurgical microscope constructed by E. Leitz.

this instrument when the object was to be photographed the prism *F* was withdrawn from the path of light and the image allowed to form on a photographic plate placed *below* (Fig. 64).

A slightly different construction is shown in Figure 67. For photographic purposes the image forms on a plate placed in a holder rigidly connected with the instru-

ment, no eye-piece being used. As the distance between the photographic plate and the objective is short, very small photomicrographs are obtained, which must generally be subsequently enlarged. *Z* is a plate carrying an eye-piece for use with the long bellows camera (Fig. 66). The Le Chatelier microscopes are constructed by Ph. Pellin of Paris.

In order to be able to examine identical portions of the same specimen at different times with the Le Chatelier microscope, Le Grix (1907) suggested the arrangement shown in Figure 68. A circular metallic disk with rectangular opening *RR'* and carrying two pointed stops *A* and *B* is fitted to the stage. A file mark *E* is made in the specimen *M*, which is then placed on the stage so that the stop *A* enters the groove *E*

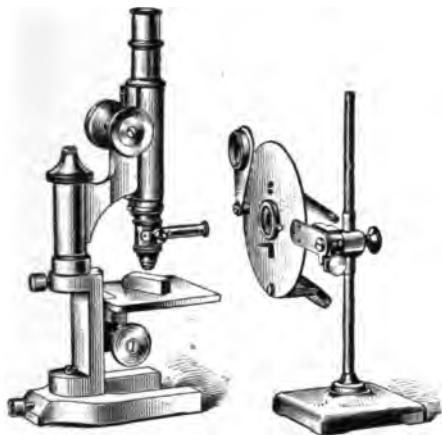


Fig. 71. — Metallurgical microscope constructed by E. Leitz.

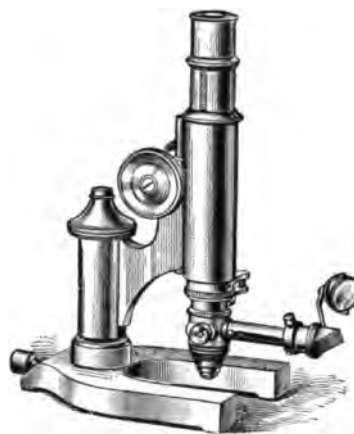


Fig. 72. — Metallurgical microscope constructed by E. Leitz.

while the specimen presses against the other stop *B*, in this way securing a constant position for the object.

Ernst Leitz. — A slightly modified form (Fig. 69) of the Le Chatelier inverted microscope is made by Ernst Leitz of Wetzlar, Germany. The modifications were suggested by Guertler. The stage and illuminating appliances are shown on a larger scale in Figure 70.

The same maker also manufactures the microscope shown in Figures 71 and 72 designed by W. Campbell. The stage can be removed and the upper part of the instrument attached to the base for the examination of large surfaces.

P. F. Dujardin. — P. F. Dujardin and Co. of Düsseldorf construct a Le Chatelier inverted microscope as shown in Figure 73. They also make the microscope (Fig. 74) in which the vertical illuminator carries its own source of light and condenser.

C. Reichert. — The metallurgical microscope (Fig. 75) designed by Professor Rejtő is made by C. Reichert of Vienna. The position of the vertical illuminator immediately below the eye-piece should be noted. The stage is provided with a leveling mechanism. The same maker manufactures an inverted Le Chatelier microscope as shown in Figure 76.

By means of a mirror *Sp* (Fig. 77) placed in the camera box it is possible to focus the image on a ground glass *M*, on the same side of the instrument as the observer,

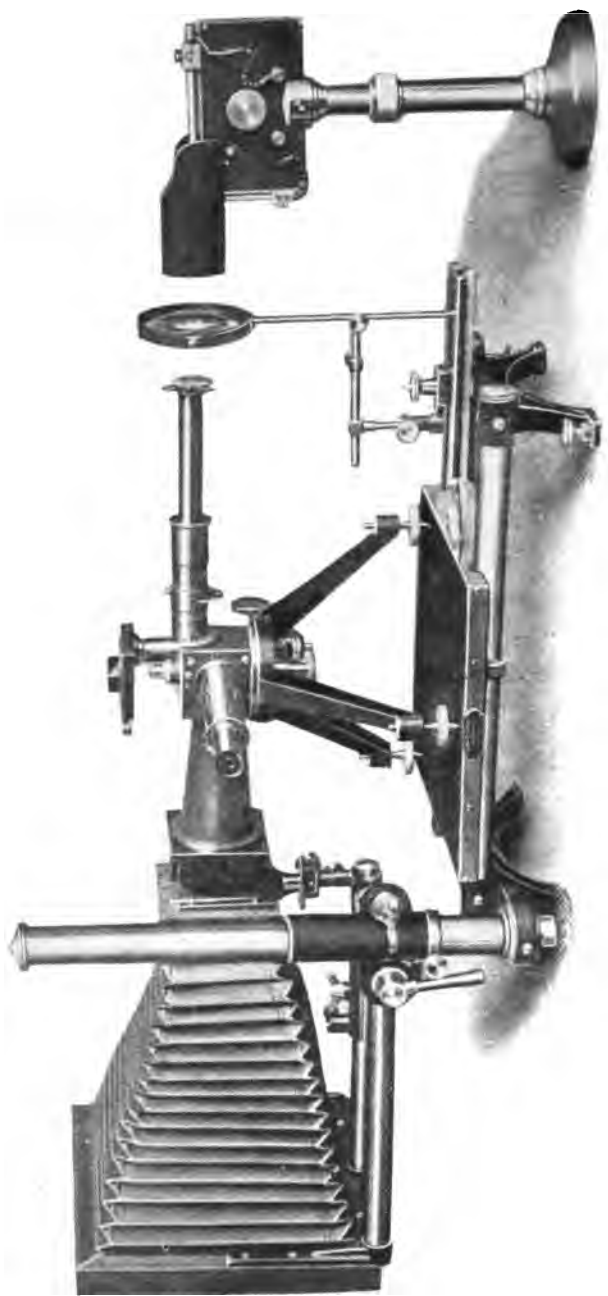


Fig. 73. — Inverted metallurgical microscope constructed by P. F. Dujardin and Co.

thereby facilitating the manipulations. During exposure the mirror which is hinged is folded close to the side *M* permitting the image to form on the photographic plate at *K*.

Robin. — The microscope and photographic attachment shown in Figure 78 was designed by Robin. Visual examination is possible only on the screen of the camera.



Fig. 74. — Metallurgical microscope constructed by P. F. Dujardin and Co.

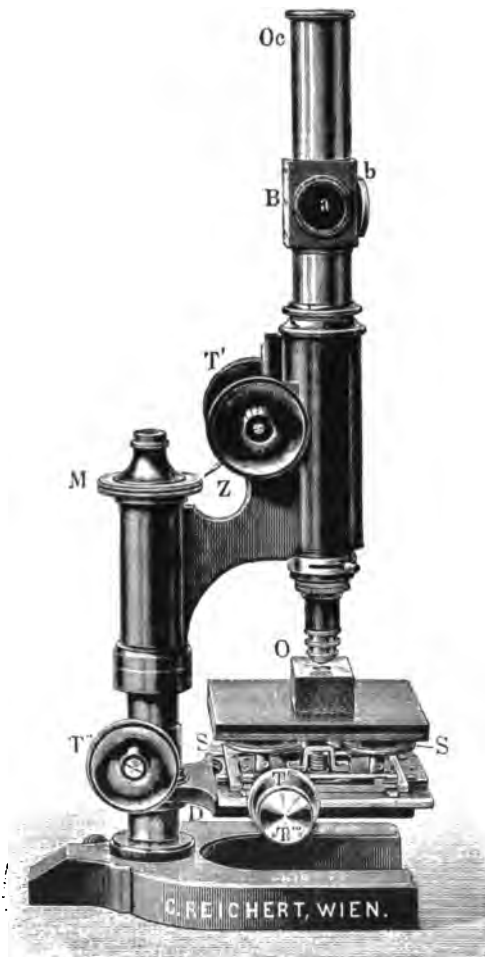


Fig. 75. — Metallurgical microscope constructed by C. Reichert.

The stage consisting of a smooth disk is tilting and the specimen is fastened upon it with wax. To secure an accurately horizontal position of the polished surface, a plug with a perfectly flat surface is screwed into the microscope in place of the objective and the stage raised until the specimen coming in contact with the plug, the latter through gentle pressure causes the polished surface to assume a horizontal position. The plug is then removed and the objective inserted.

Scientific Materials Co. — The inverted microscope and photographic attachment (Fig. 79) are made by the Scientific Materials Co.

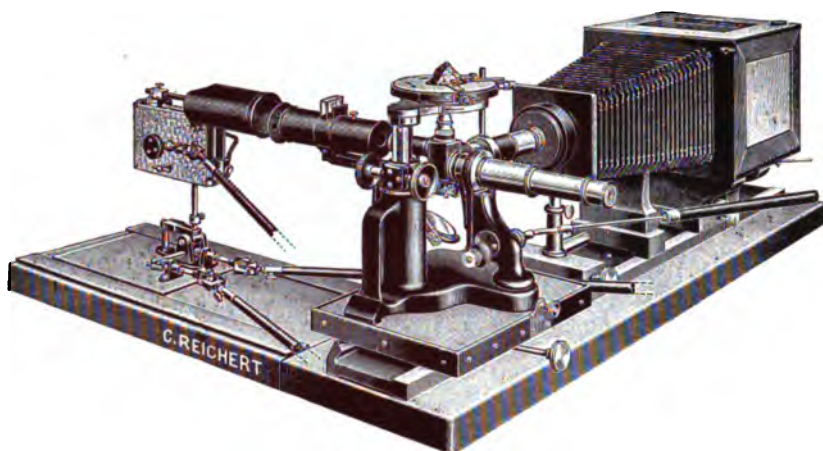


Fig. 76. — Inverted metallurgical microscope (C. Reichert.)

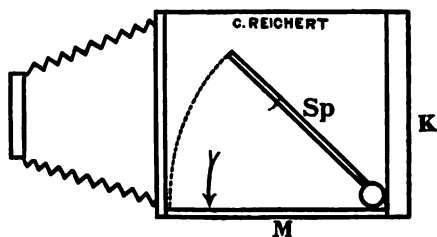


Fig. 77.

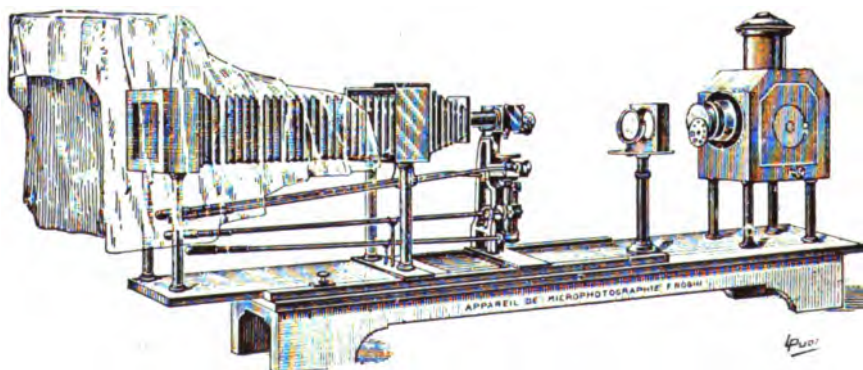


Fig. 78. — Metallurgical microscope designed by Robin.

Martens. — The Martens metallurgical microscope (1899) made by Zeiss of Jena is shown in Figure 80. It can be used horizontally only, the tube is very wide and the vertical, mechanical stage is provided with both coarse and fine adjustments *Y* and *Z* and with leveling-screws *aa*. The flexible connection *f* permits the focusing

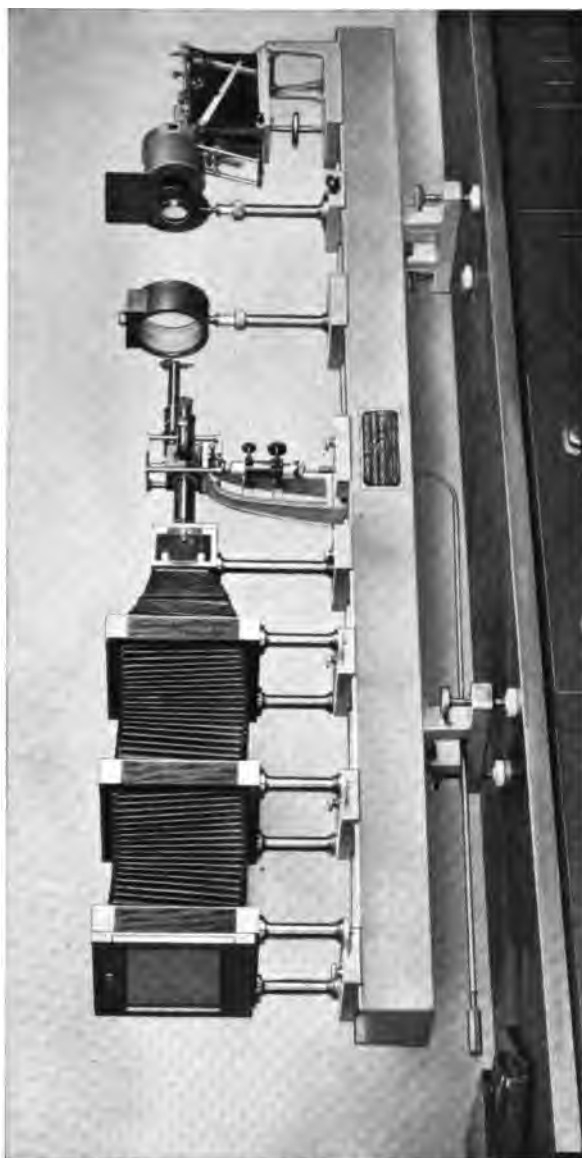


Fig. 79. — Inverted metallurgical microscope. (Scientific Materials Co.)

of the object from the camera screen. The instrument is designed especially for photography.

A complete Zeiss equipment including a large electric arc lamp is shown in Figure 81. It will be noted that the mounting of the camera is entirely separate from that of the other parts.

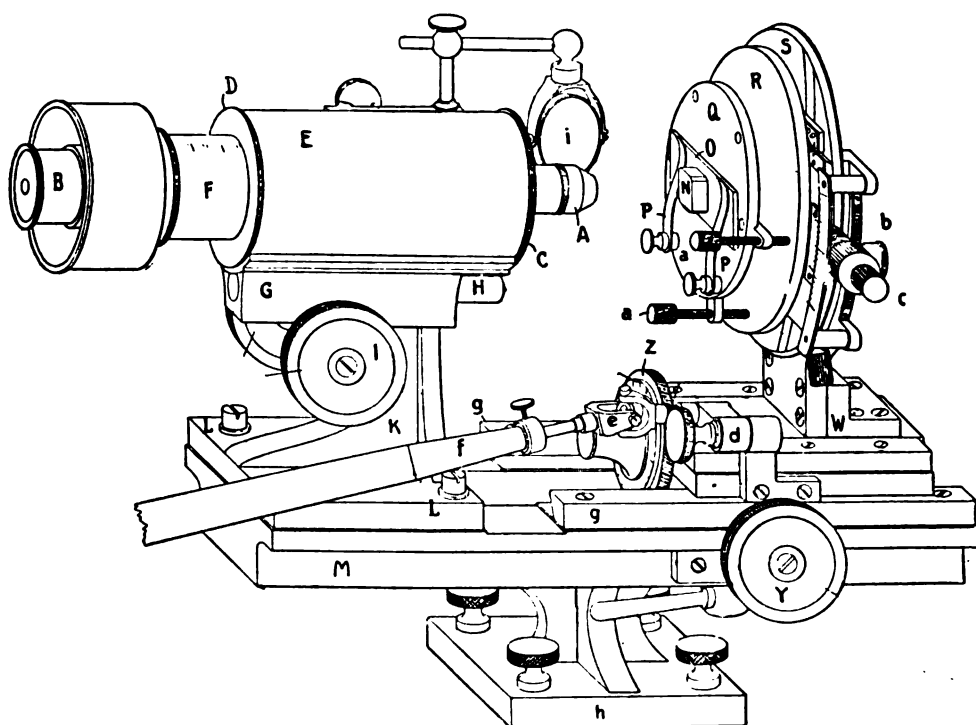


Fig. 80. — Martens metallurgical microscope.

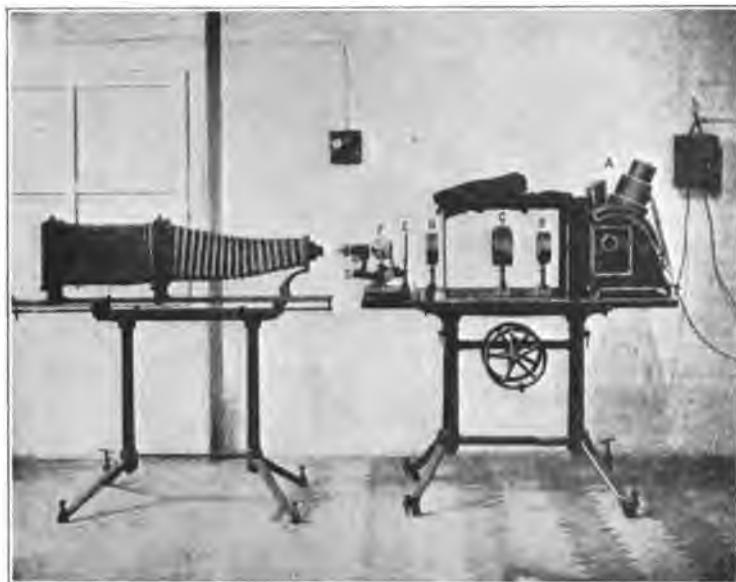


Fig. 81. — Martens-Zeiss metallurgical microscope and camera.

Rosenhain. — The microscope shown in Figure 82 was constructed by R. and J. Beck for Rosenhain. The stage is mechanical and provided with coarse and fine adjustments, and all controlling heads are placed beneath. Appliances are provided



Fig. 82. — Rosenhain metallurgical microscope.

for various kinds of illumination. The necessary alteration of focus for photographing can be done at the eye-piece by a suitable arrangement provided for that purpose.

Osmond. — Osmond used a Nachet microscope of the ordinary type connected with a vertical camera and a prism illuminator. He writes, however, that special metallurgical microscopes "are certainly to be preferred." In Osmond's opinion the vertical is very much superior to the horizontal camera for studying metals.



Fig. 83. — Nachet metallurgical microscope.

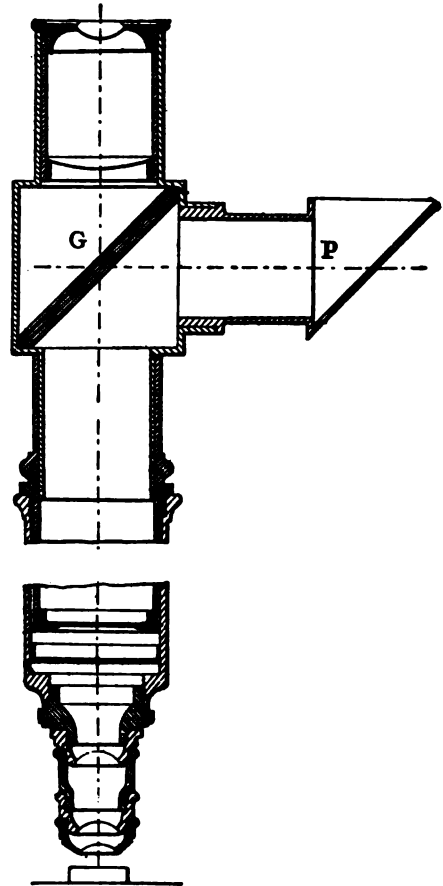


Fig. 85. — Cornu-Charpy metallurgical microscope.



Fig. 84. — Guillemin-Nachet prism illuminator.

Nachet. — Nachet of Paris constructs the metallurgical microscope (Fig. 83). The vertical illuminator carries a tube provided with an iris diaphragm. The stand is to be used in the vertical position only. The stage has a coarse vertical adjustment. A similar microscope is made with mechanical stage provided with both coarse and fine adjustments.

The prism illuminator (Fig. 84) designed by Guillemin is made by Nachet. A lateral as well as a slight tilting motion may be imparted to the prism through the milled heads *B* and *C*.

Nachet's illuminating objectives have been described and illustrated in Chapter I.

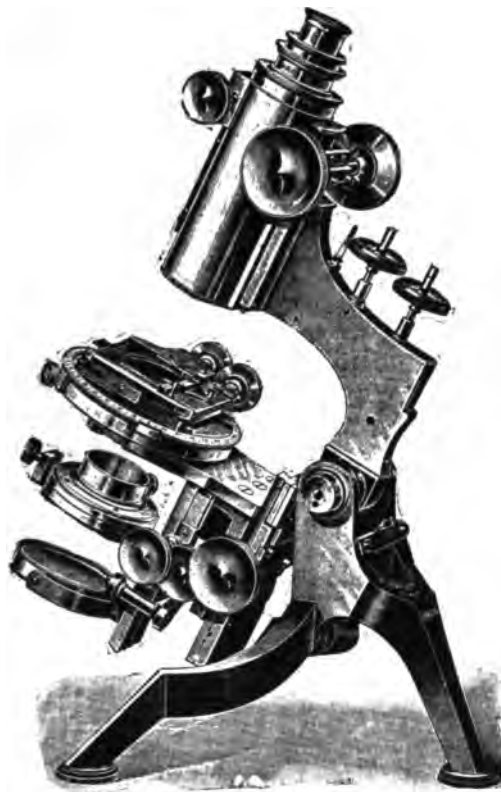


Fig. 86. — Metallurgical microscope constructed by Watson and Sons.

Cornu-Charpy. — The arrangement shown in Figure 85 was used by Charpy. The vertical illuminator *G* consists of four thin glass plates placed at an angle of 45° immediately below the eye-piece and it receives the light reflected by the totally reflecting prism *P*. This prism is so mounted that it can rotate freely around the axis of the microscope and also around the axis *GP* of the tube to which it is attached, thus making it possible to receive upon it the light proceeding from a source of light placed anywhere.

Watson and Sons. — The metallurgical microscope (Fig. 86) was constructed in 1904 by Watson and Sons of London. The stage is provided with both coarse and

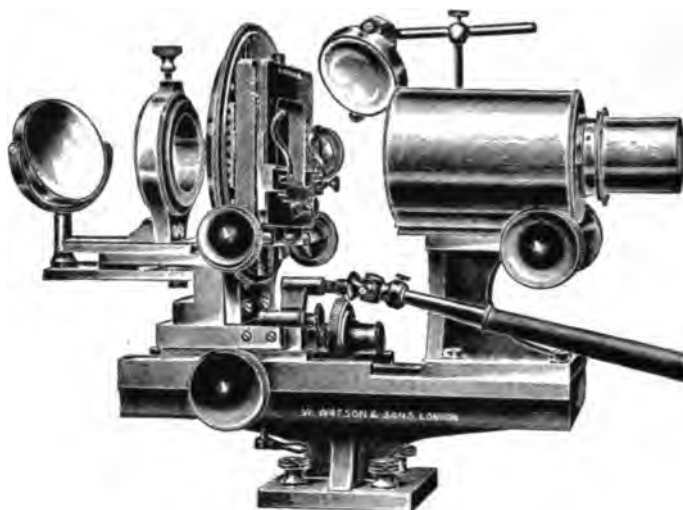


Fig. 87. — Horizontal metallurgical microscope constructed by Watson and Sons.

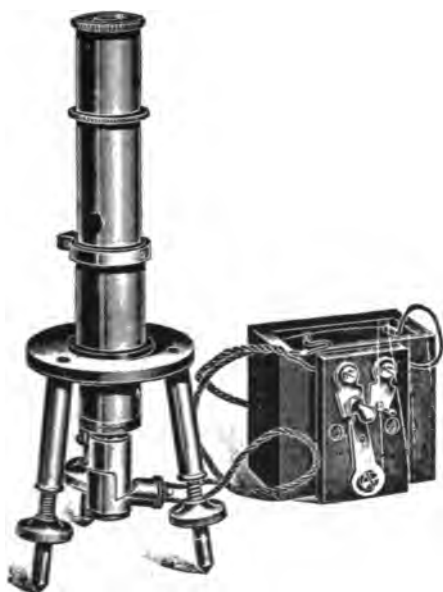


Fig. 88. — Stead's workshop microscope.
(J. Swift and Son.)

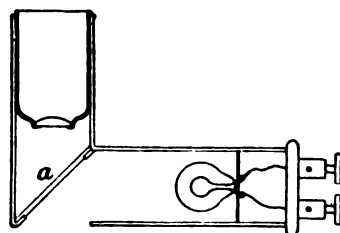


Fig. 89.

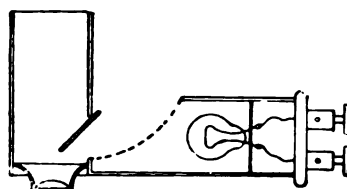


Fig. 90.

fine adjustments. The same makers following Martens construct the horizontal metallurgical microscope (Fig. 87) and also simpler and less expensive models of metallurgical microscopes, some of them provided with leveling stages.

Workshop Microscopes. — Metallurgical microscopes of simple construction, stageless, easily transportable and especially adapted to the examination of polished spots

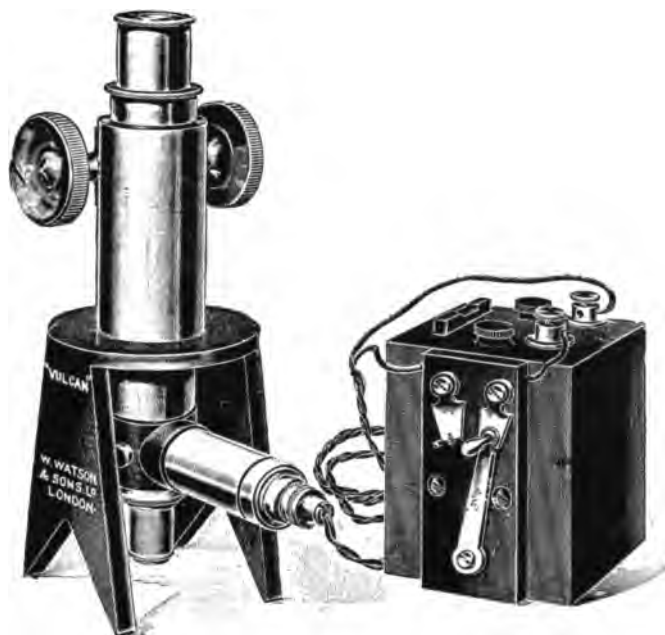


Fig. 91. — Workshop microscope. (W. Watson and Sons.)

on large pieces, in the mills or shops, are known as workshop microscopes. The model Figure 88 is constructed by J. Swift and Son according to Stead's designing. For very low-power work the lamp and vertical illuminator are placed below the objective as shown in Figure 89, while for higher power they are placed above (Fig. 90). A sim-

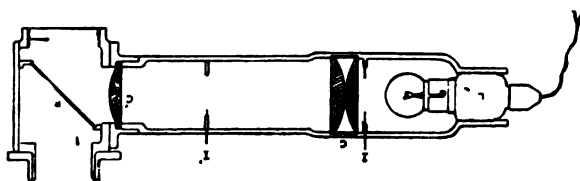


Fig. 92. — Illuminating attachment for workshop microscope. (W. Watson and Sons.)

ilar instrument (Fig. 91) is manufactured by W. Watson and Sons. The illuminating attachment is shown in Figure 92. The same illuminator may be used with any microscope for vertically illuminating opaque objects.

Workshop microscopes constructed by C. Reichert according to designs of Martens, Rejtö, and Jüptner are shown respectively in Figures 93, 94, and 95.

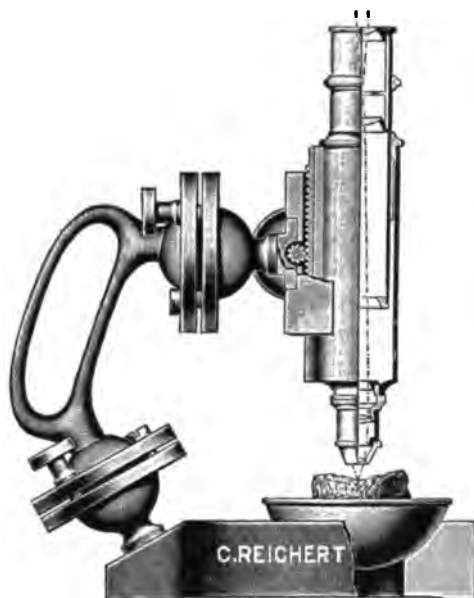


Fig. 93. — Martens' workshop microscope. (C. Reichert.)

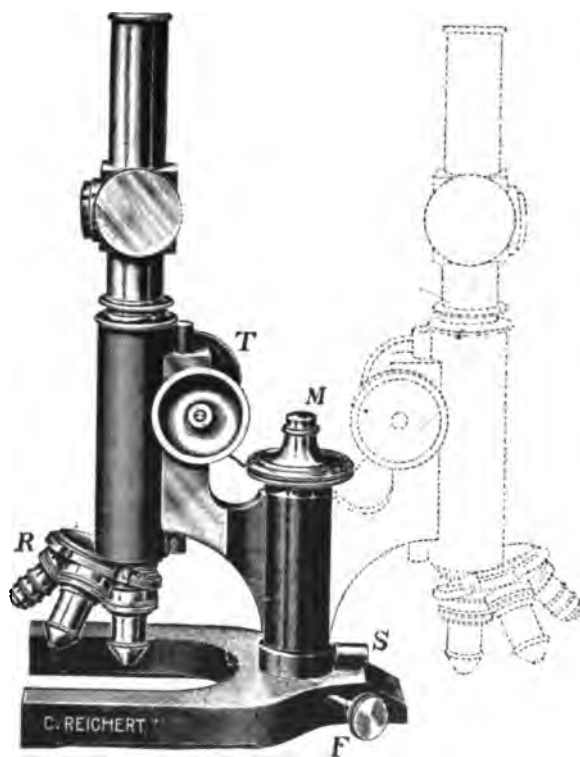


Fig. 94. — Rejtő's workshop microscope. (C. Reichert.)

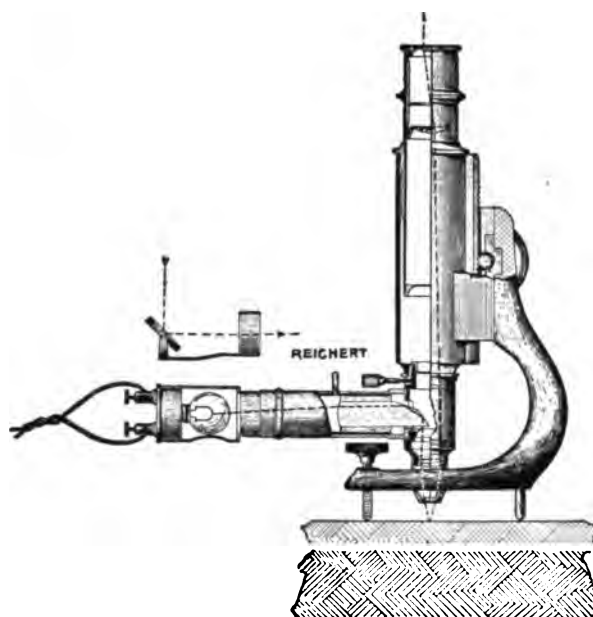


Fig. 95. — Jüptner's workshop microscope. (C. Reichert.)

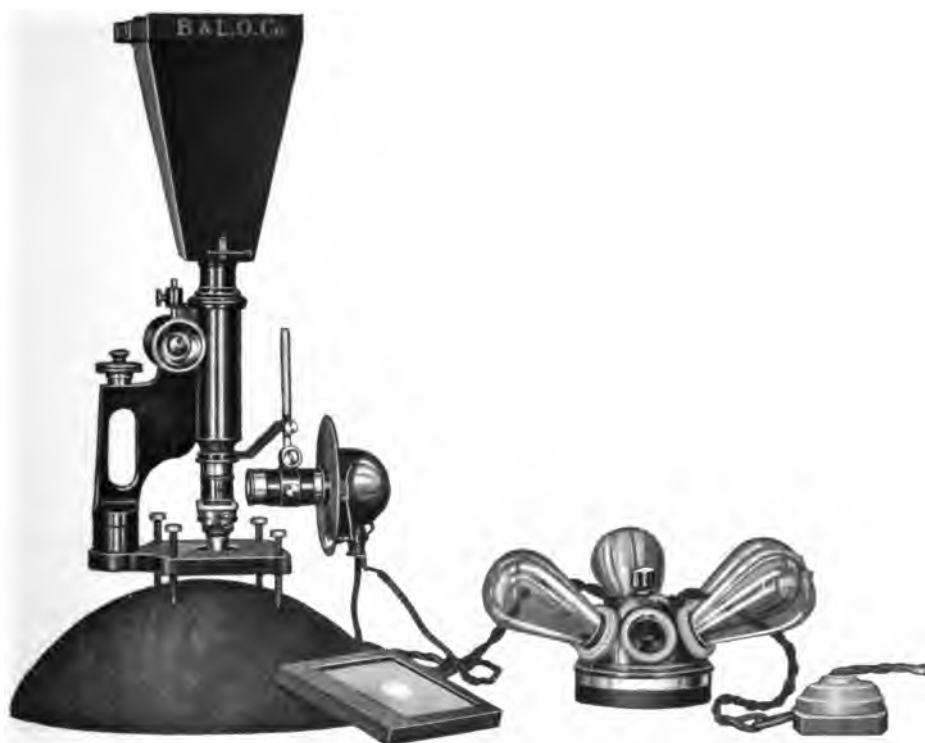


Fig. 96. — Tassin's workshop microscope. (Bausch and Lomb Optical Co.)

The Tassin workshop microscope, manufactured by the Bausch and Lomb Optical Co., is shown in Figure 96, with camera attached.

R. and J. Beck. — In 1904 R. and J. Beck of London constructed the prism vertical illuminator shown in Figure 97. The device is fitted with an iris diaphragm beneath the prism for cutting off outside light, and a plate of stops so arranged that the position of the beam of light impinging on the prism can be varied until parallel light of the right angle is obtained. The same makers construct the instrument

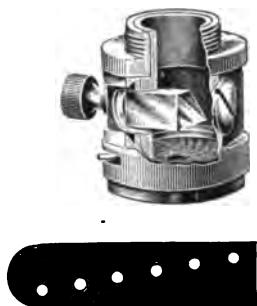


Fig. 97. — Beck prism illuminator.

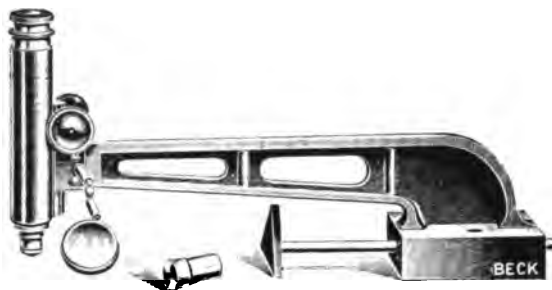


Fig. 98. — Beck surface microscope.

shown in Figure 98 for the examination of large metallic surfaces. The Rosenhain microscope described in these pages is likewise made by R. and J. Beck.

The vertical illuminator, Figure 99, is manufactured by the Bausch and Lomb Optical Co. It has two small, square mirrors, one for high power objectives, the other for low powers. The aperture in the side of the mounting is fitted with a small tube carrying an adjustable condensing lens, for focusing the light. The mirror carrier is mounted on a slide providing for oblique as well as central illumination.

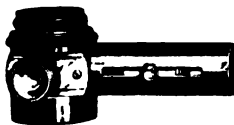


Fig. 99. — Vertical illuminator with condensing attachment. (Bausch and Lomb Optical Co.)

F. Koristka. — The prism vertical illuminator (Fig. 100) was described by F. Koristka of Milan in 1905. An iris diaphragm placed in front of the prism controls the light which it receives. By pulling out the arm carrying the prism the latter may be removed from the field.

Ph. Pellin. — The Le Chatelier inverted microscope is constructed by Ph. Pellin of Paris. The same makers also manufacture a portable microscopic outfit designed by Guillet (*Trousse de Métallographie*). It includes a small electric motor for polishing, a vertical microscope so constructed that it can be fastened to any object it is

desired to examine, files, emery-papers, etching reagents, etc. All parts are compactly placed in a carrying case.

Carl Zeiss. — The instruments used by Martens and Heyn already described in these pages are constructed by Carl Zeiss of Jena. The prism vertical illuminator made by the same firm has been described and illustrated in Chapter I.



Fig. 100. — Koristka prism illuminator.

Spencer Lens Co. — The Spencer Lens Co. of Buffalo, N. Y., manufacture a vertical metallurgical microscope with movable stage.

Bausch and Lomb Optical Co. — The microscopes and accessories used and designed by the author and fully described in Chapter I are manufactured by the Bausch and Lomb Optical Co. of Rochester, N. Y.

CHAPTER IV

PURE METALS

Microstructure. — When a properly prepared sample of a pure metal is examined under the microscope, the revealed structure generally presents the appearance of a polygonal¹ network (Figs. 101 and 102), an indication that the metal itself is composed of irregular polyhedral² grains, each mesh or polygon of the network representing a section through a polyhedron.²

Crystallization. — When a substance passes from the liquid to the solid state, the process of solidification is generally accompanied by crystallization, i.e. the molecules

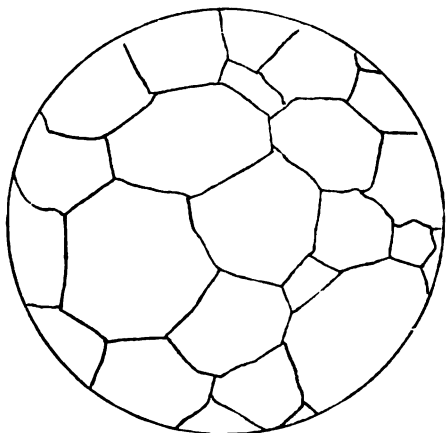


Fig. 101. — Pure gold. Cast. Magnified 50 diameters. (Andrews.)

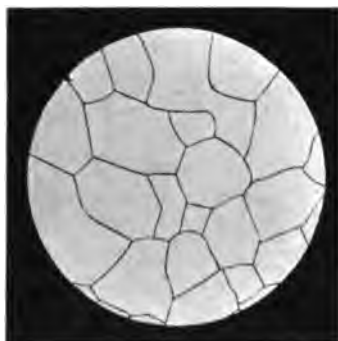


Fig. 102. — Pure copper. Magnified 8 diameters. (Houghton.)

of the substance so arrange themselves as to form small solids of regular geometrical outlines, such as cubes, octahedra,³ etc. Each of these *spontaneously* formed symmetrical solids is called a crystal and any substance made up of crystals is said to be crystalline.

Crystals possess the property of breaking more readily in one or more directions. This property is called “cleavage.” The planes of cleavage or direction of easy rupture are generally parallel to the faces of the crystals. A cubic crystal, for instance,

¹ A polygon is a closed geometrical figure with straight sides (necessarily three or more).

² A polyhedron (plural, polyhedra or polyhedrons) is a closed geometrical solid bounded by plane (smooth) faces (necessarily four or more).

³ An octahedron (plural, octahedra or octahedrons) is a geometrical solid (a polyhedron) bounded by eight plane faces.

splits readily in three planes parallel to the three sets of faces of the solid. In Figure 103, ABC, DEF, and GHI indicate the cleavage planes of a cubic crystal. The direction of its cleavage planes constitutes the orientation of the crystal.

Solid substances which are not crystalline are said to be "amorphous." They are characterized by the absence of any symmetrical grouping of their molecules. Glass is a good example of an amorphous substance.

Idiomorphic Crystals. — When the fluidity of a substance and other conditions are such that the formation and growth of the crystals are given free play, perfect (and sometimes very large) crystals are produced. These perfect crystals, with faultless geometrical outlines, perfect cubes for instance, are called "idiomorphic" crystals.

Allotriomorphic Crystals. — When the free development of crystals is hindered by less favorable crystallizing conditions, such for instance as collision or contact with other crystals, likewise in process of formation, the regular external form is not preserved and the resulting imperfect crystals are called "allotriomorphic" crystals, also,

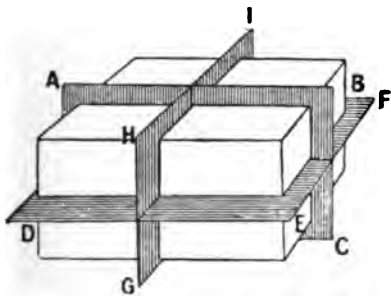


Fig. 103. — Cleavage planes.
(Mellor.)

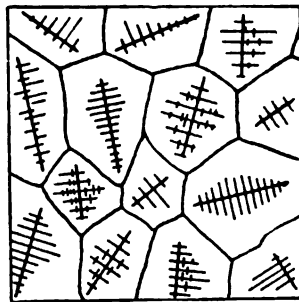


Fig. 104. — Crystallization from
centers. (Desch.)

but more seldom, "anhedrons" or faceless crystals. Such crystals are said to have taken their shape from their surroundings. It should be noted, however, that allotriomorphic crystals, like idiomorphic crystals, are composed of crystalline matter. An allotriomorphic crystal may be regarded as resulting from the mutilation of an idiomorphic crystal, the mutilation affecting the external shape only, and not the crystalline character of the substance.¹

Crystallization of Metals. — Metals when they solidify generally give rise to the formation of allotriomorphic crystals. The explanation for this is to be found in the fact that crystallization sets in simultaneously at many different centers (see Fig. 104). From each center a crystal grows through successive addition of crystalline matter similarly oriented, until meeting with other surrounding crystalline growths, radiating from other centers, the free development of its external form is arrested. The mechanisms of this crystalline growth has been clearly illustrated by Rosenhain (Fig. 105). Five stages of the progressive growth of the grains are shown in *a* to *e*, while in *f* the final polygonal outline of the grains is indicated. The polygonal networks shown in Figures 101 and 102, representing the structure respectively of pure gold and pure copper, do not indicate, therefore, cleavage planes, i.e. outlines of true crystals,

¹ Crystalline groups or aggregates of allotriomorphic crystals are sometimes called "crystallites" while if they assume some distinct form they may be further described as "dendrites" or "tree-like," "fern leaves," "star-like crystallites," "crystalline grains," etc.

but merely boundaries or junction lines between adjacent crystalline growths or "grains." They mark the regions where neighboring crystalline growths collided with resulting distortion of their external forms. Some believe, as explained later, that a little amorphous metal is left at the boundaries.

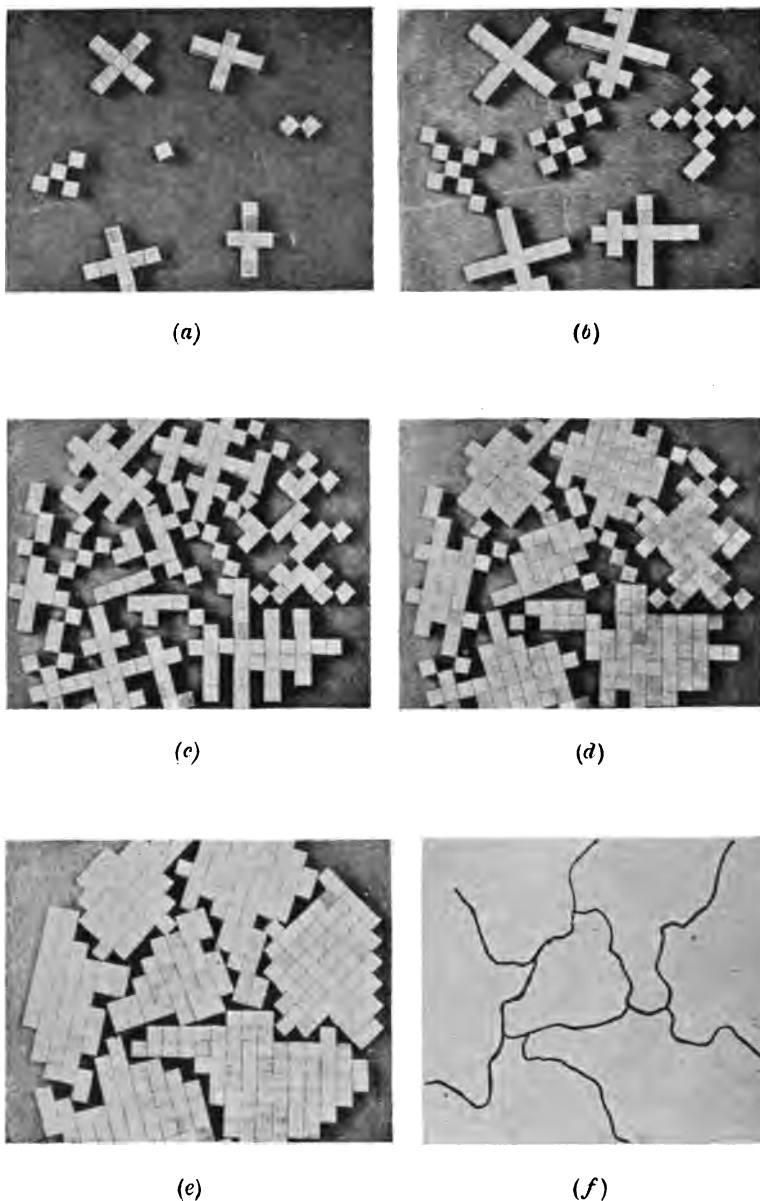


Fig. 105. — Illustrating the growth of crystalline grains. (Rosenhain.)

The number of crystalline grains of which a certain mass of metal is composed must depend, therefore, upon the number of centers or nuclei at which crystallization begins and this in turn probably depends upon the metal itself, its rate of cooling and,

according to some, its purity; the slower its solidification and the greater its purity the fewer the nuclei and therefore the larger the crystalline grains.

Grains of Metals. — If crystallographers were interested in the constitution and structure of metals they would undoubtedly refer to the small polyhedral grains of which they are composed as allotriomorphic crystals. This expression, however, although the only scientifically correct one, does not appeal to metallurgists, who generally call these imperfect crystals “crystal grains,” “crystalline grains,” or even simply “grains.” The expression crystalline grains which is quite common appears satisfactory since it suggests the two main facts to be remembered as to the nature of the grains, (1) that they are not perfect crystals and (2) that they are nevertheless crystalline. Dana himself writes that cast iron is made up of *crystalline* grains. He



Fig. 106. — Pure copper. Magnified 125 diameters. (F. C. Langenberg in the author's laboratory.)

says further: “Crystallization produces masses made of crystalline grains when it cannot make distinct crystals.” Nor is there very great objection if, for the sake of brevity, the word grain alone be used, bearing in mind once for all the crystalline character of metals.

To render the polygonal boundaries of crystalline grains visible under the microscope the highly polished metallic surface must generally be treated by an acid or some other chemical reagent capable of dissolving or corroding the metal, with or without deposition of a film of some precipitated matter. According to Ewing these boundaries are made evident by the differential action of the acid which produces differences of level by attacking one grain more energetically than its neighbors. Each of the short sloping surfaces which connect one grain with another appears black under vertical illumination because it does not reflect the light back into the tube of the microscope.

Another explanation of the nature of these boundaries is offered later.

Crystalline Orientation of the Grains. — A slight chemical attack or etching of the polished samples brings out merely the polygonal structure described and illustrated in the preceding pages. If the etching be somewhat deeper, however (through the use of a stronger reagent or because of a longer attack), it is observed that the polygons or meshes of the network are differently colored (Fig. 106), some appearing very dark, others less dark, others still, brilliant. This heterogeneousness in the appearance of sections through adjacent grains is due to the fact elucidated above that *each grain, i.e. each allotropic crystal, is made up of crystalline matter similarly oriented in the same grain but differently in different grains*. Bearing this in mind the dissimilarity of coloration between contiguous grains is readily explained, for if the



Fig. 107. — Typical etching figures of pure metals. (Gulliver.)



Fig. 108. — Part of a crystalline grain of bismuth. Magnified 5 diameters. (Gulliver.)

crystalline matter of any individual grain is so oriented that it reflects the incident light into the microscope-tube, that grain will appear bright, while, on the contrary, if its orientation is such that the light is reflected outside the microscope, the corresponding grain will appear dark. By slightly inclining the sample in various directions, or by rotating it, some of the grains that were bright become dark, being, so to speak, extinguished, while some of the dark grains become brightly illuminated, because in so doing we change the direction of the light reflected by each individual grain section. Similar results are obtained by changing the direction of the incident light. The kaleidoscopic effect just described affords a conclusive proof of the crystalline nature of metals and of the correctness of the explanation offered to account for the dissimilar appearance, as to color, of contiguous grains.

Cubic Crystallization of Metals. — Etching Pits. — By still deeper etching of the polished surfaces of pure metals, it is sometimes possible to bring out clearly the crystalline character of the individual grains (see Fig. 107). The figures thus outlined, in reality small cavities, are often called “etching pits” or “etching figures.” These figures frequently correspond to sections of cubes or of geometrical solids derived

from the cube, indicating that most metals crystallize in the cubic system (also called regular, or isometric, or monometric system).¹

In Figure 108 is seen after Gulliver part of a single grain of bismuth. It is clearly made up of small crystals of geometric form.

Summary. — Summing up the indications obtained by the microscopical examination of polished and etched surfaces of pure metals, it has been shown (1) that a slight etching outlines the polygonal boundaries of adjacent crystalline grains, (2) that a deeper etching imparts different colorations to the various polygons or grain sections, a phenomenon which is due to the constancy of crystalline orientation in any individual grain and to the change of orientation as we pass from one grain to the next, and (3) that a still deeper attack often brings out clearly pits of distinct geometrical forms, often cubic, indicating that the majority of metals crystallize in the cubic system.²

The Amorphous Cement Theory and the Boundaries of Crystalline Grains. — According to a recent theory of Rosenhain and Ewen the boundaries between adjacent grains are not merely surfaces of contact but narrow spaces filled with amorphous metal or cement holding the grains together. This hypothesis is an extension of Beilby's theory of the existence of an amorphous state in metals caused by mechanical straining as outlined elsewhere. The authors argue that if the various crystalline grains were merely held together by surface contact the boundaries should be weaker than the mass whereas on the contrary fractures generally occur through the crystalline grains instead of following their outlines. Howe, however, pertinently asks why, following the author's reasoning, the surfaces of contact between the grains and the surrounding amorphous cement membranes should not be as many planes of weakness which the fractures should follow. In other words why should the contact between a crystalline mass and an amorphous mass of the same metal form a stronger union than contact between two crystalline masses of that metal.

Rosenhain writes: "where the constituent crystals of a metal meet, thin films of residual liquid will remain under conditions rendering them incapable of crystallizing so that they constitute thin films of undercooled³ liquid or amorphous metal acting as intercrystalline cement . . . When two differently oriented crystals meet, there must be a region between the two orientations, where the material cannot assume the orientation of either . . . The fundamental fact is the marked strength of crystal boundaries in pure metals."

The formation of amorphous films between two crystalline grains is graphically represented, according to Rosenhain, in Figure 109. *A* and *B* are sections through two adjacent grains while the shaded portion between them represents the residual liquid which remains amorphous on solidifying.

The existence of amorphous crystalline cement accounts for the greater strength

¹ The other crystallographic systems are the hexagonal, the tetragonal, the orthorhombic, the monoclinic, and the triclinic.

² We have other indications of the cubic crystallization of metals such for instance as the hexagonal character of many of the polygons which crystallographers consider to be due to interfering cubes and octahedra (the octahedron is a form belonging to the cubic system). Again, under favorable crystallizing conditions nearly perfect cubes have been obtained in the case of several metals.

³ The undercooling of a substance means its cooling to a temperature lower than that at which a certain transformation should normally take place without inducing that transformation. Water for instance cooled below its freezing point without causing the formation of ice is in an undercooled condition, or to express it differently, it is in a "metastable" equilibrium.

and toughness of a fine-grained structure seeing that it must contain a greater quantity of strong amorphous cement. It will be shown also that it affords an explanation of the alteration of many of the properties of pure metals when subjected to thermal and mechanical treatments.

The difference between Beilby's and Rosenhain's amorphous cements, however, should not be overlooked: the former results from the severe straining of crystallized metal, the latter from the solidification of liquid layers enclosed in such narrow spaces that they cannot assume a crystalline orientation. From the well-supported contention, therefore, that Beilby's cement exists and that it is strong, hard, and brittle it does not necessarily follow that Rosenhain's cement possesses similar properties or indeed that it exists at all.

Straining of Metals. — Slip Bands. — Ewing and, later, Ewing and Rosenhain through some skilfully conducted experiments and convincing reasoning have re-

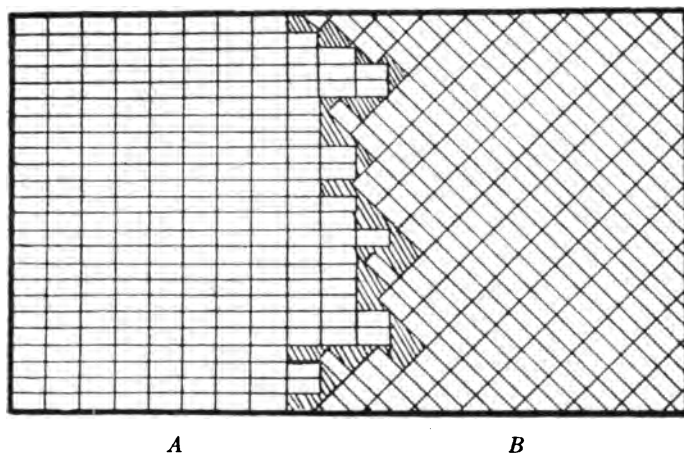


Fig. 109. — Section through two adjacent crystalline grains. (Rosenhain.)

vealed the character of the strain produced in a pure metal by the action of a stress which may eventually cause its rupture.

Polished sheets of metals were strained very gradually while being examined under the microscope. When the yield point is reached, i.e. when plastic deformation begins to occur, black lines are seen to cross the crystalline grains of which the metal is made up. These lines are generally quite straight and are parallel in the same grains but have different directions in different grains. Figure 110 shows the appearance under vertical light of Swedish iron strained by tension, magnified 400 diameters.

As the strain increases other systems of lines, inclined to the first, make their appearance and eventually two, three, and even four systems of intersecting lines may be seen in each grain.

These lines are not cracks but steps in the surface, which steps are due to slips along the cleavage or gliding planes of the crystals.¹ In Figure 111, *AB* represents the

¹ According to Humfrey the crystal properties of cleavage and gliding are in many ways distinct, and do not necessarily occur with maximum readiness along the same crystallographic planes. This difference probably occurs in the case of crystals of iron, which have been shown to possess cubic cleavage planes, but octahedral gliding planes.

polished surface of two grains, *C* the junction line between these two grains. The pull takes place in the direction of the arrows.

Yielding occurs by finite amounts of slips at a limited number of places, *a*, *b*, *c*, *d*, *e*, resulting in short portions of inclined cleavage or sliding surface appearing black

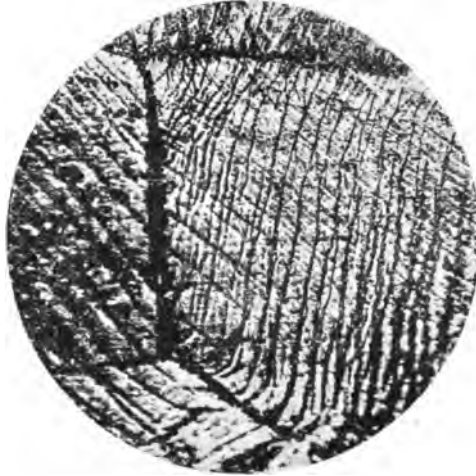


Fig. 110. — Slip bands in Swedish iron strained by tension. Magnified 400 diameters. (Ewing and Rosenhain.)

under the microscope, because they do not send back any light into the tube. By oblique light some of these slip bands appear black while others are bright. When the surface is rotated some of the bands which were black become bright and vice versa owing to the change of their position in regard to the incidence of the light,

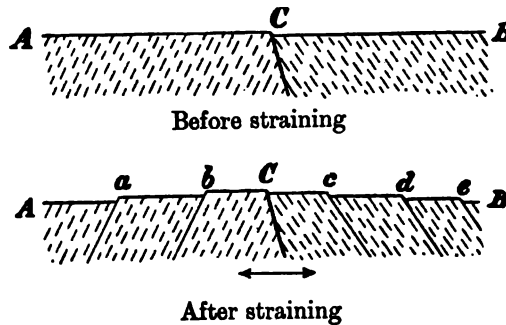


Fig. 111. — Diagram illustrating the effect of strain upon the structure of metals and alloys. (Ewing and Rosenhain.)

which is conclusive proof that the black lines are not cracks, but inclined surfaces as described above.

It is seen then that, contrary to the general belief, metals remain crystalline after the severest strain, and that the flow or plastic strain in metals is not a homo-

geneous shear such as occurs in the flow of viscous fluids, but is the result of a limited number of separate slips, the crystalline elements themselves undergoing no deformation.

The Amorphous Cement Theory and the Straining of Metals. — Beilby has conclusively shown that during the polishing of metals with very fine powders thin layers of amorphous metal are produced considerably harder than the metal itself and necessarily severely strained. Osmond and Cartaud had previously made a similar observation. If it be accepted that an amorphous condition may be produced on the surface of a polished specimen through the mechanical straining of the polishing operation, it is a logical conclusion that in the cold working of metals the severe straining which that operation induces will likewise produce layers of amorphous metal or cement between the surfaces of adjacent crystals or along the gliding planes of crystals which have undergone the slipping described by Ewing and Rosenhain.

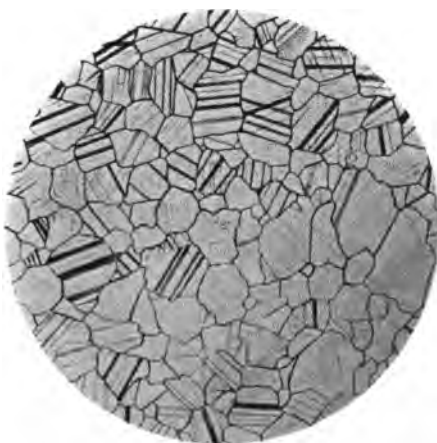


Fig. 112. — Twinnings in marble (caused by pressure). Magnified about 5 diameters. (Bayley.)

To the formation of this cement may be ascribed the marked changes of properties accompanying the cold working of metals, such as increased tenacity and hardness, decreased ductility and density, etc.

According to Tamman and others the crystalline deformations caused by mechanical straining are sufficient to account for the altered properties of cold-worked metals, it being unnecessary to conceive the formation of films of amorphous cement covering the gliding surfaces after the slipping process.

Humfrey having observed the behavior of slip bands in the vicinity of the grain boundaries and assuming the existence of intercrystalline cement, writes: "All the observations demonstrate the resistance to plastic deformation by slip which occurs at the crystal junctions, and suggest the idea that each crystal is surrounded by and firmly attached to a continuous skin, which, while hard and plastically undeformable, is yet thin and capable of elastic bending and stretching . . . The state of affairs can best be conceived by imagining that after overstrain each crystal is enclosed and held within a stretched skin holding it so as to oppose further strain in the same direction."

Twinning and Twin Crystals. — By twinning is meant the grouping of two or more crystals or parts of crystals in such a way that they are symmetrical to each other with respect to a plane between them (the twinning plane) which plane, however, is not a plane of symmetry. Twins result generally from a portion of a crystal



Fig. 113. — Twinnings in copper produced by straining followed by annealing. Magnified 125 diameters. (F. C. Langenberg in the author's laboratory.)

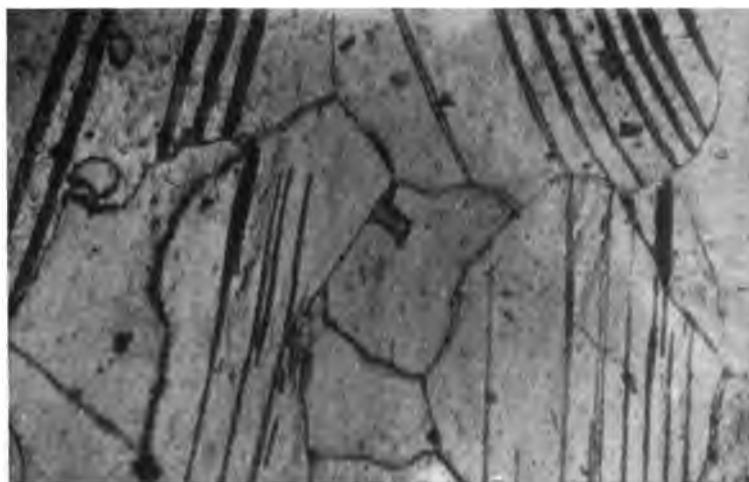


Fig. 114. — Lines of Neumann in a low carbon steel sheet. Magnified 100 diameters.

turning by a definite angle, say 180 deg. They are sometimes produced by straining alone (Fig. 112), when they are called mechanical twins, but more often by straining followed by annealing. Many metals after such treatments contain numerous twins (Fig. 113). The production of twin crystals in the complete absence of strain is doubtful.

Lines of Neumann. — The crystalline grains of metals are sometimes found to be crossed by a number of parallel lines or bands (Fig. 114) called "Lines of Neumann" and which might at first be taken for slip bands but which, according to Osmond and Cartaud and others, are undoubtedly mechanical twins. They follow the orientation of the grains. Lines of Neumann can be distinguished from slip bands by repolishing and etching the sample, when slip bands do not reappear while the lines of Neumann do.

Influence of Mechanical Treatment. — Metals are frequently subjected to powerful pressure exerted by rolls, presses, hammers, etc., with a view of producing metallic objects of desired shapes. This treatment affects the structure and, therefore, the properties of the metal. Roughly speaking such vigorous kneading has a tendency to reduce the size of the final grains, either through preventing the formation of large grains or by breaking up or distorting preëxisting grains. A smaller grain in turn generally implies greater ductility (provided it be not distorted) and often greater strength. The effect of work upon the structure and properties of commercial iron and steel will be duly considered.

Influence of Thermal Treatment. — The size of the crystalline grains of pure metals varies in different metals even when cast and cooled under identical conditions. Their dimension is generally affected also by the rate of cooling during solidification and, therefore, by the size of the casting, since a large casting will cool more slowly than a smaller one.

The common belief is that the prolonged exposure of pure metals to a high temperature (annealing) tends to enlarge the grains, the enlargement being the greater the higher the temperature, the longer the time of exposure, and the slower the cooling. While such growth undoubtedly takes place in the case of commercial and, therefore, impure metals, at least after straining, it is held by some metallurgists that in absolutely pure metals the grain will not grow on annealing even after straining.

This view is based upon a theory brilliantly conceived by Ewing and Rosenhain and supported by the results of skilfully conducted experiments. These scientists argue that even so-called pure metals always contain a certain amount of impurities, and that even a very minute amount of impurity would suffice to form a thin but practically continuous film of eutectic in the crystalline boundaries. They contend "that there is constant diffusion from the surface of the crystal into the eutectic and equally constant re-deposition of metal upon the crystal from the eutectic. If there are several crystals in contact with the same eutectic, there will be, under some conditions, a state of dynamic equilibrium between them, the amount dissolved from each being exactly counterbalanced by the amount deposited upon it; if, however, there is any difference in their solution pressure in respect to the eutectic, then the less soluble will grow at the expense of the more soluble. The metal constituting the eutectic films being much nearer its melting-point than the rest of the mass, would thus be favorable to comparatively rapid diffusion, but the rate of such diffusion, and, consequently, the rate of growth of crystals, would be enormously increased by heating the metal to a temperature above the melting-point of the eutectic in question."

The theory proposed depends upon the existence of a difference in the solubility of the two crystal faces in contact with the eutectic film. The only difference between these two faces is, apparently, in the orientation of the crystalline elements, but this difference is sufficient, in the authors' opinion, to produce a difference in their rate of solution in the eutectic film, seeing that it results in such marked difference in their solubility in the etching acid, which, as is well known, attacks some grains much more readily and deeply than neighboring ones whose elements have another orientation. To account for the influence of the orientation of the elements upon the solubility of the crystals, the authors suggest to extend to alloys the electrolytic theory of solution. "Such differential actions," they say, "may most probably be attributed to differences of electrical potential in the

surfaces involved. If we accept this view of the matter, then the diffusion across films of eutectic becomes a case of electrolysis."

This theory explains why only strained crystals of the metals examined will grow, while unstrained crystals show no tendency to change, even at high temperatures. "The explanation, on the electrolytic theory, is that in the unstrained state the crystals are surrounded by practically continuous films of eutectic, and that electrolysis only becomes possible when severe distortion has tinuous through these films in places, allowing the actual crystals to come into contact; the electrolytic circuit would than be for each pair of crystals, from one crystal to the other by direct contact and back through the eutectic film."

If the authors' conception be true, recrystallization by annealing in a perfectly pure metal would not occur but, as they rightly say, it is almost hopeless to obtain a sample of metal sufficiently pure to prove or disprove the theory. They argue, however, that if the growth of crystals is due to the presence of a eutectic film between them, the absence of such film would be a barrier to all such growth, and that a weld between two clean-cut surfaces should show no growth of crystal across the weld. This they actually proved to be so in the case of lead.

If they are right, it likewise follows that in metals contaminated by impurities with which they form solid solutions there should be no growth of grains on annealing, because of the absence of the needed eutectic film.

The remarkable crystalline growth of very low carbon steel after severe straining followed by annealing at suitable temperatures, described in another chapter, is a striking instance of the action of straining (cold working) in promoting grain growth in subsequent annealing.

Notwithstanding Ewing and Rosenhain's strong argument, satisfactory evidences are still lacking in support of the contention that both straining and the presence of impurities are necessary conditions to grain growth on annealing. So far as the matter has been investigated it does seem that the grain of a pure metal will not grow unless it has been previously strained, but that it must also contain some eutectic forming impurities has not been satisfactorily demonstrated.

Amorphous Cement Theory vs. the Heat Treatment of Pure Metals. — It is believed by Rosenhain and Ewen that the amorphous films cementing together the crystalline grains of pure metals act as a vehicle for crystal growth under suitable temperature conditions. This intercrystalline amorphous cement might play the part ascribed to eutectic films in Ewing and Rosenhain's earlier theory. While according to the former theory the grains of strictly pure metals could not grow on annealing, even after straining, owing to the absence of eutectic films, the amorphous cement theory permits such growth and this is in better harmony with observed facts.

The annealing of cold-worked metal should result in the transformation of some of the strong but hard and brittle cement resulting from the cold working, as previously explained, into crystallized metal and this should be accompanied by decreased hardness and increased ductility, thus accounting for the well-known influence of annealing on cold-worked metal.

Impurities. — It is well known that the addition of surprisingly small amounts of impurities or foreign substances often affect very greatly some of the most important properties of metals, such as their strength, ductility, fusibility, electrical conductivity, etc., and we naturally look for correspondingly marked changes of structure. In order to understand this important influence of impurities upon the properties of metals it will be necessary to consider at some length the nature of the union which exists between the metal and the impurity. Let us first note that by impurity we mean a *very small proportion* of some foreign substance which may be any other metal, a metalloid, or a definite compound.

The metal or metalloid contaminating the metal may (1) remain uncombined or (2) it may combine with some (generally a small amount) of the metal to form a definite chemical compound. The uncombined contaminating metal or metalloid or resulting chemical compound may then (a) be soluble in the solid metal forming with it a "solid solution" or (b) be insoluble in the solid metal in which case it is rejected by the crystalline grains, in the form of an eutectic alloy.

The meaning of the expressions "solid solutions" and "eutectic alloys" should now be explained. As Professor Howe has well expressed it the essential features of an ordinary liquid solution are (1) a complete merging of the constituents and (2) in indefinite proportions. By complete merging is meant a union so intimate that the separate existence of the constituents cannot be detected by any physical means, such for instance as microscopic examination under the highest magnification. The homogeneity of the substance is such that it resists any physical attempt at breaking it. The merging moreover must remain complete and absolute for varying proportions of the constituents, for it is evident that if it existed only for certain well-defined proportions of the component parts, the resulting substance would be of the nature of a definite chemical compound and not of a solution.

Bearing in mind these characteristics of ordinary solutions, we find that in some substances, while passing from the liquid to the solid state, the constituents remain completely merged and in indefinite proportions. *The essential characteristics of liquid solutions are retained in the solid state.* Hence the name of solid solutions given to such substances. A common and excellent example of solid solutions is found in the case of glass in which the three usual constituents, silica, lime, and alkali, are so completely merged that their existence cannot be detected by physical means; the microscopical examination of glass under the highest magnification fails to reveal the presence of its component parts. Glass on solidifying passes from the condition of a liquid solution to that of a solid solution. Many metals likewise form on solidifying solid solutions, i.e. they solidify into a mass so absolutely homogeneous that the identity of the component metals is entirely lost. The union between some metals and metalloids also frequently forms solid solutions.

It is held by some crystallographers that in order to form solid solutions the uniting substances must be "isomorphous," that is, must be capable of yielding crystals of the same form, hence the name of "isomorphous mixtures" frequently given to solid solutions.¹ The homogeneous crystals formed by solid solutions are often called "mixed crystals" — and that expression is frequently used as an equivalent for solid solution. There are some crystallographers, however, who believe that isomorphism of the constituents is not essential to the formation between them of solid solutions, and that the use, therefore, of isomorphous mixtures as synonymous of solid solution is not warranted. The use of the expression "mixed crystals" is likewise to be discouraged because it suggests a mixture, and therefore, heterogeneity, which is precisely contrary to the nature of solid solutions.

Considering now those impurities, whether metals, metalloids, or definite compounds, which form solid solutions with the metal they contaminate, it is found

¹ If isomorphism favors the formation of solid solutions, as it undoubtedly does, seeing that most metals are isomorphous, we naturally infer that they will readily form solid solutions. We now know that such is the case, for if metals are not generally soluble in each other (when solid) in *all proportions* there are few instances of metals entirely insoluble in each other in the solid state. The formation of solid solutions between metals is therefore very frequent.

as might have been expected that their presence has no great influence upon the character of the structure. Suitably prepared surfaces of such impure metals still exhibit the polygonal network structure characteristic of pure metals. The small polyhedra of which the impure metal is composed, however, are now allotriomorphic crystals of a solid solution instead of a pure metal. While the character of the structure remains the same, the dimension of the grains may be markedly affected, by the presence of a small amount of impurity forming a solid solution with the metal.

The second group of impurities, namely those foreign substances, whether they remain or not uncombined, which do not form solid solutions with the contaminated metal may usually be readily detected under the microscope as they are generally rejected to the grain boundaries during the process of solidification (or afterwards) as shown in Figure 115. These insoluble impurities are not, however, rejected as such by the crystalline grains, but on the contrary unite *mechanically* with a small amount

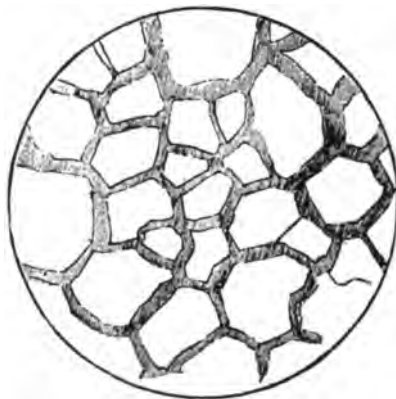


Fig. 115. — Gold containing 0.20 per cent lead. Magnified 100 diameters. (Andrews.)

of the metal to form what is known as an “eutectic alloy,” that is an alloy of lowest melting-point, and it is this alloy which is expelled by the solidifying grains. The formation and nature of eutectic alloys will be considered at greater length in a subsequent chapter.

It will be apparent that those contaminating substances which fail to be dissolved by the metal, may form actual membranes surrounding each grain, the membranes being of the nature of an eutectic alloy. As might be anticipated, the presence of such membranes, whether continuous or not, have generally a very marked influence upon the properties of the metals, frequently decreasing their ductility, weldability, electrical conductivity, etc., and often increasing their fusibility, hardness, etc.

The rejection during solidification and subsequent cooling of those impurities which fail to be retained in solid solution by the metal, to the grain boundaries or other crystallographic planes, reveals the crystalline forms of the grains themselves. The location of these impurities affords additional evidence of the cubic crystallization of metals. It will be shown later that the cubic crystallization of iron is in this way clearly revealed.

The above remarks are of a very general character and refer more especially to the behavior of impurities while the metal solidifies. In the majority of cases no further changes take place in the nature of the constituents as the metal cools to atmospheric temperature, i.e. the constituents formed on solidification are those found in the metal after complete and slow cooling. In some instances, however, and notably in the case of iron and its usual impurities, carbon, silicon, phosphorus, manganese, and sulphur, some important changes take place at temperatures considerably below the solidification point of the metal which will be duly described at the proper time.

Some writers believe that in slightly impure metals the impurities may form nuclei from which crystal growth may start, thus accounting for the apparent fact that slightly impure metals have often smaller grains than metals of greater purity. This assumption demands an early solidification of small particles of impurities within the liquid metal and, therefore, can be true only in the case of foreign substances having a higher melting point than the metal itself. It is not easily conceived how it can be applied to impurities forming solid solutions with the metal, since they then solidify together, nor to impurities forming eutectic alloys, since such alloys constitute the constituent of last solidification.

CHAPTER V

PURE IRON

Chemically pure iron is not a commercial product. It can only be obtained in small quantities by carefully conducted laboratory manipulations when, even with the most refined care, it is quite impossible to produce it absolutely pure. Until quite recently the purest commercial iron was of Swedish origin and contained as much as 99.8 per cent of iron. A commercial product known as "American Ingot Iron"¹ is now manufactured which the makers claim to contain 99.94 per cent of

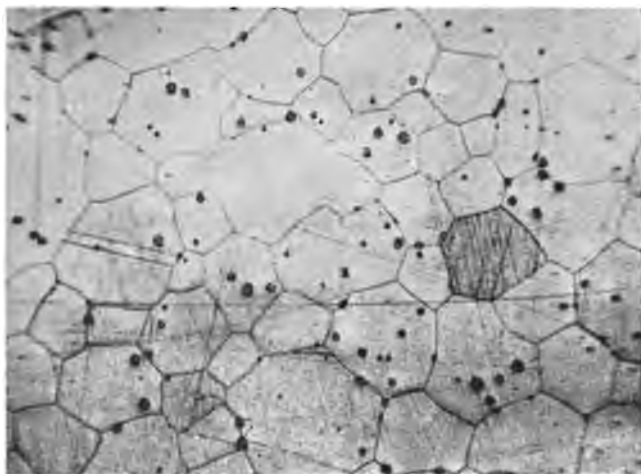


Fig. 116. — Electrolytic iron. Magnified 75 diameters. Slightly etched.
(Sherard Cowper-Coles.)

iron. Iron, or rather very low carbon steel, of a high degree of purity is also produced at the present time through refining in electric furnaces. Finally iron has been obtained in relatively large quantity, by electrolytic deposition, of a degree of purity exceeding 99.9 per cent iron.

¹ The expression "ingot" iron is applied to iron containing very little carbon, obtained molten and, therefore, cast, after removal from the furnace, whereas by wrought iron is meant iron (also generally low in carbon) obtained pasty and, consequently, always containing a certain amount of slag. Barring the presence of slag in wrought iron, both ingot iron and wrought iron may have identical chemical compositions. The expression ingot iron is seldom used in the United States, where iron obtained in a liquid state, and containing little carbon, is called low or very low carbon steel, or mild, very mild, extra mild steel, or again soft, very soft, dead soft steel.

Microstructure. — When a sample of nearly pure iron is suitably prepared and examined under the microscope some regions can readily be found absolutely free from carbon and slag and exhibiting, therefore, the structure of the pure metal. Such structure is illustrated in Figure 116 after a slight etching of the polished surface. It will be noted that it is similar to the structure of pure gold and of pure copper

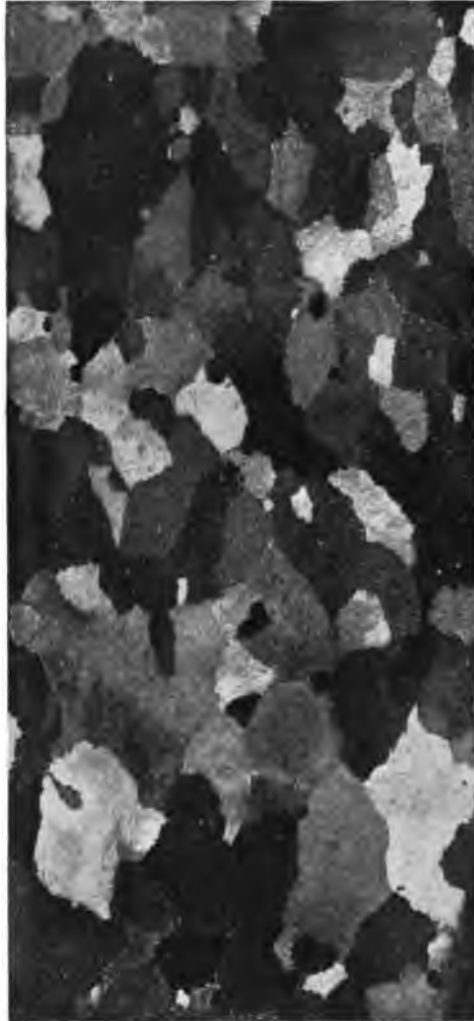


Fig. 117. — Ferrite grains. Natural size. Etched 10 minutes in nitric acid (1 to 10 water). (Stead.)

described in the preceding chapter: like gold and copper and, indeed, like most metals, iron is made up of polyhedral crystalline grains (allotriomorphic crystals). Upon deeper etching the dissimilarity, as to coloration, of adjacent iron grains is clearly brought out as shown in Figure 117. As explained in Chapter IV, this appearance is due to the fact that the grains of iron are composed of crystalline elements having the same orientation in the same grain but different ones in different grains.

As explained in the preceding chapter it is believed by some that the crystalline grains of iron like those of other pure metals are surrounded by thin membranes of amorphous cement (the network in Fig. 116) holding the grains together, this amorphous metal being harder and stronger but less ductile than the crystalline grains themselves. Before this theory had been advanced it was universally assumed that

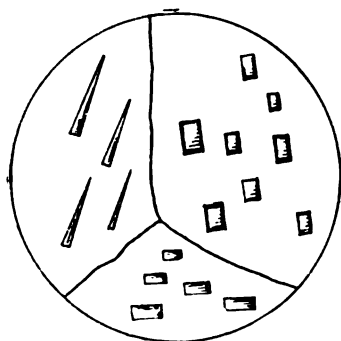


Fig. 118. — Etching pits in iron. (Desch.)



Fig. 120. — Silicon steel, 4.5 per cent silicon. Magnified 60 diameters. Part of a single grain. Etched 3 hours in nitric acid (1 to 10 water). (Stead.)

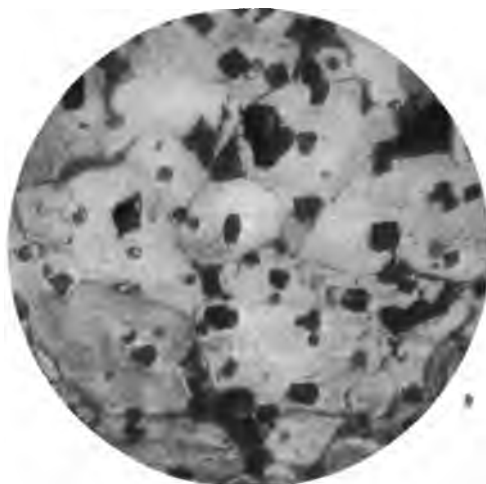


Fig. 119. — Etching pits in ferrite. (J. F. Hoyland, Correspondence Course student.)

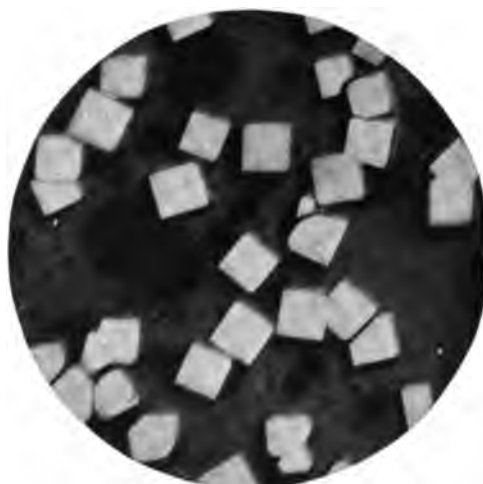


Fig. 121. — Cubic crystals of iron. Magnified 250 diameters. Obtained through the reduction of ferrous chloride. (Osmond.)

the grains were held together by surface contact alone or cohesion and that the network revealed on etching merely indicated sections through these contact surfaces made apparent owing to slight differences of solubility of adjacent grains (because of their different orientation) and resulting in slight differences of level after etching.

Cubic Crystallization of Iron. — A still deeper etching indicates clearly the cubic character of the crystallization of pure iron. This is illustrated diagrammatically in Figure 118 and by means of a photomicrograph in Figure 119. It will be noted that

the etching pits are similarly oriented in the same grain but that the orientation in adjacent grains differs. As seen in Figure 118, the etching figures may appear as triangular wedges. This occurs when the section cuts the small cubes of a grain at a certain angle, i.e. when it cuts obliquely a corner of each cube. This cubic structure is further illustrated in a remarkable manner in Figure 120, in the case of iron containing $4\frac{1}{2}$ per cent of silicon after etching three hours in dilute nitric acid. The photograph shows a portion of a single grain, hence the constancy of orientation noted. The presence of so much silicon apparently favors the development of a coarse cubic crystallization.

Osmond, through the reduction of ferrous chloride and the crystallization of the resulting metallic iron, obtained perfect isolated cubic crystals (Fig. 121). Finally almost perfect cubes have been separated by Stead from a large granule of phos-



Fig. 122. — Cubic crystals of phosphoretic iron. Magnified 5 diameters. Phosphorus 0.75 per cent, carbon 0 per cent. (Stead.)

phoretic iron (Fig. 122). Another indication of the cubic crystallization of iron is found in the occurrence of large crystallites (Fig. 123), generally resembling pine trees, in cavities of large castings of iron and steel, under conditions, therefore, favorable to the free development of crystals, these crystallites being composed of small octahedra, a crystalline form of the cubic system. Finally it will be shown later that the structural location of some of the impurities generally present in commercial iron affords further proof of the cubic crystallization of iron.

Ferrite. — Mineralogical names have been given to the constituents of iron and steel, and pure iron, or rather carbonless iron, considered as a microscopical constituent has been called "ferrite," a name suggested by Prof. H. M. Howe and universally adopted.¹ Pure iron, therefore, is composed of polyhedral crystalline

¹ This constituent was called "free iron" by Sorby, who was the first scientist to describe the microscopical structure of iron and steel.

For further description of the nature and properties of ferrite see the report of the Committee of the International Association for the Testing of Materials, "On the Nomenclature of the Microscopic Substances and Structures of Steel and Cast Iron" in the Appendix. Stead has suggested that when ferrite consists only of pure iron it should be called "ferro-ferrite."



Fig. 123. — Iron crystallite about half natural size. (Tschernoff.)

grains of ferrite. It will be seen in subsequent chapters that the ferrite of commercial grades of iron and steel is not pure iron, but rather iron holding in solid solution small amounts of silicon, phosphorus, and possibly other impurities.

Allotropy of Iron. — The study of the crystallization of iron is complicated by the existence of several allotropic forms of that metal.

Physicists and chemists do not agree as to the exact meaning of allotropy, still less as to the phraseology by which it should be defined. Allotropy certainly implies marked and sudden reversible changes taking place in some of the properties of a substance at certain critical temperatures excluding formation or dissociation of chemical compounds and changes of state although the latter might be considered as major instances of allotropy. Opinions differ, however, as to whether a well-defined change in a single property constitutes a proof of allotropy, while some scientists insist that unless a crystallographic change is observed at the critical temperature the transformation cannot be considered as an allotropic one.¹ Again it is claimed by some and denied by others that a spontaneous evolution of heat on cooling at a certain critical temperature and absorption of heat on heating at the same or nearly the same temperature is sufficient proof of an allotropic change. Others still consider the occurrence of a sudden dilatation on cooling and contraction on heating as the best criterion of the existence of allotropy. Finally, in discussing the allotropy of iron it has been attempted by some writers, arbitrarily it would seem, to exclude magnetic changes from those indicative of allotropy.

Many substances undergo allotropic changes. It is a matter of common knowledge, for instance, that sulphur exists under two distinct conditions, namely, as prismatic sulphur and as octahedral sulphur, the prismatic form being the one stable above 95.6 deg. C. and the octahedral, the stable form below that critical temperature. On heating octahedral sulphur it begins to change into the prismatic form at the temperature of 95.6 deg. and, likewise, on cooling, prismatic sulphur begins to pass to the octahedral form at that temperature. Many of the physical properties of sulphur (crystalline form, specific heat, heat of combustion, etc.) undergo sudden changes as the substance passes from one allotropic form to another.

At those critical temperatures which mark the passage of one allotropic form into another, spontaneous evolutions of heat take place on cooling and spontaneous absorptions of heat on heating. These thermal disturbances indicate a change of internal energy which when not accompanied by changes of state or by chemical changes are in the author's opinion evidences of allotropy. The usual method of detecting the existence of such thermal critical points will be described in another chapter.

Osmond's momentous discovery of the existence of two thermal critical points in pure iron respectively at about 768 and 900 deg. C. was at first accepted as proving the occurrence of iron under three allotropic varieties, γ (gamma) iron stable above the upper critical point, β (beta) iron stable between the two points, and α (alpha) iron stable below the lower point. The allotropic character of gamma and alpha iron is still universally accepted, and indeed has been firmly established, but it is contended by some that the condition of iron between its two critical points does not differ allotropically from its condition below its lower critical point; in other words that the belief in beta iron as a distinct allotropic variety should be abandoned. This important question will be considered at greater length in the chapters of this book

¹ The property of some substances of crystallizing in more than one form is called polymorphism. The expression, however, should not be used as an equivalent of allotropy.

dealing with the Thermal Critical Points of Iron and Steel, with the Hardening of Steel and with the Equilibrium Diagram of Iron-Carbon Alloys, when it will be shown that these opposite views result apparently from different conceptions as to the nature of allotropy. For our present purpose it will be assumed that iron exists, as first described by Osmond, under three allotropic conditions.

Solidification and Crystallization of Pure Iron. — As should be expected the passage of one allotropic form into another implies corresponding and, generally, sudden changes in many of the physical properties of iron. Gamma, beta, and alpha iron differ widely in regard to many of their physical characteristics. It is only desired in this chapter, however, to inquire into the possible differences of crystallization



Fig. 124. — Twinnings in gamma iron.
Magnified 200 diameters. (Osmond.)

which may exist between the three allotropic conditions of iron, leaving for later consideration the modification of the other properties.

Osmond and, later, Osmond and Cartaud have carefully investigated the difficult problem of the crystallization of the different allotropic forms of iron. Their conclusions were (1) that the three allotropic forms of iron crystallize in the cubic system,¹ (2) that octahedra are the prevailing crystalline forms of gamma iron, (3) that the cube is the prevailing form of beta and of alpha iron, (4) that beta and alpha iron are capable of forming isomorphous mixtures (solid solutions), (5) that gamma iron does not form isomorphous mixtures with beta or alpha iron.

We also have the statement of Osmond that the transformation of gamma iron into beta iron appears to include a change in the planes of symmetry, at least in carburized iron.

Again it has been shown by Osmond and confirmed by other investigators that the occurrence of twinnings is frequent in gamma iron (Fig. 124), while beta and alpha iron are free from it.

¹ In Le Chatelier's opinion there is no proof of the cubic form of gamma iron. He thinks that the facts observed are contrary to that hypothesis and that it is more probable that gamma iron is rhombohedral or orthorhombic.

It follows from Osmond's experiments that the allotropy of iron could not be proved by its crystallography, since the thermal critical points are not accompanied by changes in the crystalline form of iron. While, however, in the instances of allotropy which have been noted and studied allotropic changes are generally accompanied by changes of crystalline forms, it does not by any means follow that any allotropic transformation must necessarily imply a crystalline change.

Bearing in mind the existence of three allotropic conditions of iron, let us follow in our imagination the crystallization of iron during solidification and its subsequent cooling to atmospheric temperature. On solidifying iron crystallites are formed consisting of octahedral crystals of gamma iron. Upon further cooling below the solidification point, no change of crystalline form should take place unless it be the granulation described by Belaiew (Chapter XIII) until the first critical temperature (900 deg. C.) is reached when the iron changes from the gamma to the beta condition.

Does this allotropic change affect the preexisting crystallization of gamma iron or does it consist merely in a transformation *in situ* of each crystalline grain of gamma iron into a grain of beta iron, retaining the original external form of the gamma grain, and leaving undisturbed, therefore, the polygonal structure observed under the microscope? It may reasonably be supposed that the allotropic transformation takes place without affecting the external form of the crystalline grains, but in view of Osmond's statement that the octahedron is the prevailing crystalline form of gamma iron and bearing in mind that the small crystals revealed by suitable etching of pure iron are generally cubic, we naturally infer that the octahedral character of each grain of gamma iron has been obliterated, the small octahedral elements of gamma iron having been replaced by small cubic elements of beta (and later of alpha) iron. These conclusions, however, should be accepted with reserve, as we lack evidences of a very conclusive character. It has been shown that the change of gamma iron into beta iron is accompanied by an abrupt expansion of the cooling metal which expansion is followed by the normal contraction of cooling substances. We infer from this that, momentarily at least, each grain of beta iron occupies more space than its gamma iron progenitor.

At 750 deg. C. or thereabout, the iron passes from the beta to the third or alpha form. We may here ask the same questions as to the probable effect of this change upon (1) the outward form of each beta grain and (2) upon the internal crystalline structure of each grain. Since both beta and alpha iron crystallize in the cubic system, the cube being the prevailing crystalline form of both, and since, according to Osmond, they are isomorphous, that is capable of forming solid solutions, it seems probable that the change of beta to alpha iron affects neither the external form nor the internal crystalline arrangement of the beta grains; in other words that each small cubic element of beta iron is converted bodily (although probably gradually and not abruptly) into a cubic element of alpha iron.

If the above represents the real mechanism of the allotropic changes, it will be evident that the polyhedral grains revealed through the etching of polished sections of pure iron were formed during solidification and consisted originally of gamma iron, these grains having retained their external shape while undergoing allotropic transformation, but having probably undergone at the upper critical point an internal change, the octahedral form of the crystalline elements having been replaced by the cubic form.

Rosenhain and Humfrey by straining a bar of iron heated to a high temperature

at the center (the temperature, therefore, decreasing towards both ends) have made evident the existence of three distinct kinds of distortions with sharp lines of demarcation between them, corresponding in all probability to the distortion respect-

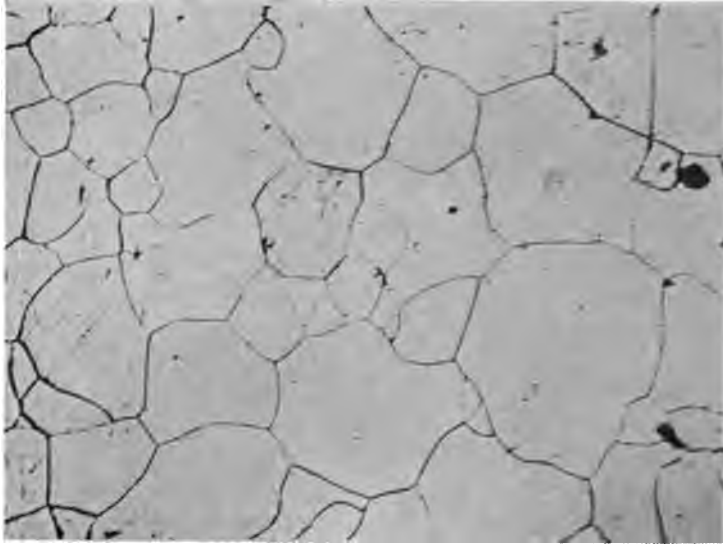


Fig. 125. — Iron before straining. (Rosenhain.)



Fig. 126. — Same as Fig. 125 but strained. (Rosenhain.)

ively of gamma, beta, and alpha iron. The estimation of the temperature of different portions of the bar by means of fusible salts appears to sustain the authors' contention thus furnishing an additional support, and a substantial one, to Osmond's brilliant theory of the allotropy of iron.

Nevertheless information of a more positive and concordant nature is still needed to settle to the satisfaction of all the question of the relation between the thermal critical points of pure iron and possible crystallographic changes.

Twinnings and Neumann Lines. — It has been already stated that according to Osmond and Cartaud twin crystals frequently occur in gamma iron. It will be shown later, however, that gamma iron which exists normally only above the upper critical point of iron requires for its preservation at atmospheric temperature the presence of a considerable amount of carbon, if not, also, of other elements such as manganese and nickel. The twin crystals of gamma iron shown in Figure 124 do not refer to pure gamma iron but to gamma iron containing a considerable amount of nickel.

Iron or at least very low carbon steel not unfrequently exhibits the presence of Neumann lines which as previously stated are probably mechanical twins. In Figure 114 an interesting instance of the occurrence of such lines has been shown.

It has been mentioned in the preceding chapter that in order to distinguish between slip bands and Neumann lines the specimen should be repolished and again etched, a treatment which should result in the reappearance of the Neumann lines but not of slip bands since the latter are merely slight differences of level erased by the polishing operation.

Strains and Slip Bands. — It has been shown by Ewing and Rosenhain that like other metals, iron when subjected to a strain exceeding its elastic limit yields through a succession of small crystalline slips readily distinguishable on a polished surface as one or more systems of parallel lines (Figs. 125 and 126). It has been observed by these authors that this slipping occurs most readily along octahedral planes from which it would seem to follow, as already noted, that these gliding planes are not identical to cleavage planes since the latter are cubic.

According to Humfrey the slip bands which form first are confined almost entirely to the central parts of the crystals and only spread gradually towards the boundaries as the straining becomes more severe when they show a tendency to become narrower and to bend so as to meet them at a smaller angle.

As explained in Chapter IV it is believed by some that the severe straining of the iron crystals at the gliding planes must result in the formation of thin layers of amorphous metal and that this theory affords a satisfactory explanation of the marked influence of cold working on the physical properties of iron.

Influence of Mechanical Treatment. — Like that of other metals the structure of iron is affected by mechanical work. Undisturbed cooling being a necessary condition to the free development of crystals, it will be evident that if the metal be vigorously worked, that is subjected to powerful mechanical pressure, while cooling from a high temperature, the formation of crystalline grains will be greatly hindered or preexisting crystals broken or distorted. The important influence of work upon the structure (and therefore upon the properties) of iron and steel will be duly considered in these pages.

Influence of Thermal Treatment. — The size of the crystalline grains of iron is affected as is the case with other metals, by the speed of its solidification and subsequent cooling, slow cooling promoting the formation of large grains. When the iron is produced in a pasty condition as in the puddling process and the charcoal hearths, the dimensions of its grains depend essentially upon the temperature from which the metal is allowed to cool undisturbed by mechanical work.

As explained in the preceding chapter, it seems probable that *pure* metals do not undergo any crystalline growth on reheating (annealing) *unless they have been previously strained*. For similar reasons we may doubt the occurrence of any crystalline growth on annealing chemically pure iron *in the complete absence of strain*. The behavior of electrolytic iron, however, presently to be described appears to oppose this view.

The possible part played, during the annealing operation, as described in the preceding chapter, by the thin films of amorphous cement believed by some to be present between the grains applies to pure iron as well as to other pure metals.

The influence of heat treatment upon the structure and physical properties of commercial irons and steels will be dealt with at length in these pages.

Crystallizing Properties of Electrolytic Iron. — Stead and Carpenter have made the important discovery that electrolytic iron of very great purity appears to possess

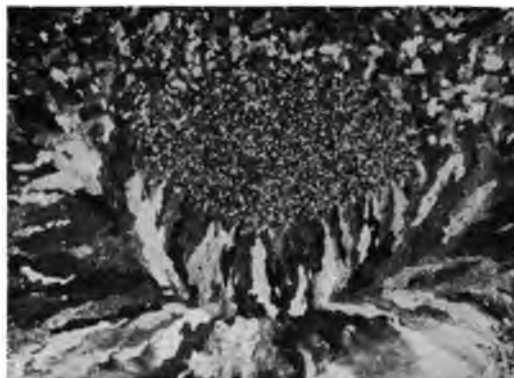


Fig. 127. — Thin sheet of electrolytic iron a portion of which was heated to 925 deg. C. for one minute and the whole sheet cooled in air. Magnified 4 diameters. (Stead.)

crystallizing properties radically different from those of other irons. When sheets of electro-deposited iron not exceeding 0.012 in. thick (preferably not over 0.01 in.) are heated above the upper critical point of iron and then cooled below that point enormous crystals are formed in three seconds after cooling below the critical point. The coarse crystals are sometimes “equi-axed” and sometimes “radial,” but according to their discoverers there is no reason for thinking that they are constitutionally different. This remarkable crystalline phenomenon is well illustrated in Figure 127, which represents, under a magnification of only four diameters, the structure of a strip of electrolytic iron heated to between 920 and 930 deg. C. for one minute and cooled in air. It was then cleaned with hydrochloric acid, dipped into strong nitric acid, washed, and dried. The central portion where the crystals are small represent a portion which was not heated above the upper critical point, its structure remaining unaltered. The lower portion of the strip is composed of what the authors called “radial” or “columnar” crystals of great size, while in the upper part of the strip the ordinary polyhedral or “equi-axed” crystals have formed. The sharp boundaries

between the fine-grained unaltered metal and the portions having assumed a coarse crystallization should be noted.

The authors write that once the coarse crystals are formed they cannot be destroyed except either by cold mechanical work, or by heating above the upper critical point followed by quenching, or by a very extended heating above that point followed by slow cooling. They add that very prolonged heating above the upper critical point followed by slow cooling does not result in the formation of coarse crystals.

Bearing in mind that above its upper critical point iron exists in the gamma allotropic form, the above phenomenon seems to indicate that on cooling through its upper point the small crystals of gamma iron existing above it are converted into very large crystals of beta iron, or if we doubt the existence of beta iron, then of alpha iron, which is the view held by Stead and Carpenter. The striking features of this extraordinary crystalline transformation are (1) the fact that unless the sheets be very thin (less than 0.012 in. thick) the growth does not occur, (2) the very large size of the resulting crystalline grains, and (3) the great speed with which they form.

Benedicks believes that the condition required for the occurrence of the phenomenon is extreme purity and absence of mechanical inclusions. The influence of the thickness of the sheet has been explained on the ground that in very thin sheets the crystals can grow, so to speak, only in two directions, and thus appear extremely large, although their volume may be relatively small. In other words the thinner the sheet the larger the new crystals would *appear* to be, since crystals of equal volume would necessarily occupy a larger *area* — they would be spread over a greater surface.

Influence of Impurities. — Commercial iron is always contaminated by the presence of at least five elements, namely, manganese, silicon, phosphorus, sulphur, and carbon, generally referred to, although often wrongly, as impurities. The important question of the influence of these substances upon the structure and, therefore, upon the properties of iron and steel will be fully considered in another chapter, when it will be shown that these elements form definite compounds with iron, FeSi , Fe_3C , Fe_3P , or with each other, Mn_3C , MnS , and that some of these compounds, FeSi , Fe_3P , are retained by the iron in solid solution, while others, Fe_3C , Mn_3C , MnS , are rejected to the boundaries of the crystalline grains or along other crystallographic planes, the former two giving rise to the formation of eutectoid mixtures. This behavior of the impurities of iron and steel conforms with the general behavior of impurities described in Chapter IV.

CHAPTER VI

WROUGHT IRON

Wrought iron is the name given to commercial iron free enough from carbon and other impurities to be malleable when such metal is manufactured through the reduction of iron ores or the refining of cast iron at a temperature so low that it is obtained in a pasty condition and, therefore, mechanically mixed with a considerable amount of the slag formed during the operation.

When the refining treatment is conducted at a temperature sufficiently high to deliver the resulting products in a molten condition, the refined metal which is then free from slag is called steel. Wrought iron and steel may otherwise have identical chemical composition, although usually steel contains more manganese and less silicon than wrought iron, often more carbon and less phosphorus.

Commercial iron which is not malleable is called cast (pig) iron. The modern method of producing wrought iron consists in refining cast iron in a non-regenerative reverberatory furnace (the puddling furnace), while the refining of cast iron for the production of steel is conducted (1) in the Bessemer converter or (2) in a regenerative reverberatory furnace (the Siemens open-hearth furnace). Cast (pig) iron is the result of smelting iron ore in blast-furnaces.

Wrought iron is sometimes called "puddle" or "puddled" iron, from the name of the furnace in which it is now generally manufactured. Wrought iron made in the old charcoal hearths either directly from the ore or from pig iron (Catalan, Lancashire, or Walloon processes) is called "charcoal hearth" or "charcoal" iron. Wrought iron produced in the puddling furnace from small pieces of steel scrap is known as "bush-eled" iron, apparently from the fact that the small pieces of steel used can be gathered in bushel baskets. The product resulting from the reheating to a welding heat and subsequent working of piles (fagots or faggots) of pieces of wrought iron and steel scrap is called "fagoted" iron, also spelled "faggoted" iron. Knobbled iron is wrought iron produced by the knobbling process which resembles the South Wales process in which pig iron is first melted down in a coke refinery, considerable silicon and carbon being eliminated, and then treated in a charcoal hearth somewhat as in the Lancashire process.

Puddled iron and charcoal hearth irons are generally freer from manganese than fagoted and bush-eled irons, while charcoal hearth iron generally contains less phosphorus and less slag than puddled iron. In England wrought iron is also called malleable iron.

When wrought iron contains enough carbon to be hardened by quenching it was at one time called wrought steel, but this expression is now obsolete.

In the puddling process the pasty lumps of iron removed from the furnace at the end of the operation are called "puddle (puddled) balls" while the roughly elongated

masses resulting from the squeezing of puddle balls are sometimes called "blooms." The blooms are rolled into "muck bars," or "puddle (puddled)" bars. The product resulting from the cutting, piling, heating, and rolling of muck bars is known as "refined iron," "refined bar," "merchant bar," "single rolled iron," "single refined iron," or "No. 2 iron"; if subjected to a second piling, heating, and rerolling, as "double (doubly) refined iron," "double rolled iron," "No. 3 iron," "best bar," "wire iron," or also "refined bar." (H. P. Tiemann.)

Chemical Composition. — Wrought iron contains, besides an appreciable amount of slag, a small proportion of carbon and small quantities of the usual impurities, manganese, silicon, phosphorus, and sulphur.

Microstructure of Longitudinal Section. — Upon being withdrawn from the puddling furnace, the white hot, pasty balls of wrought iron are subjected to vigorous

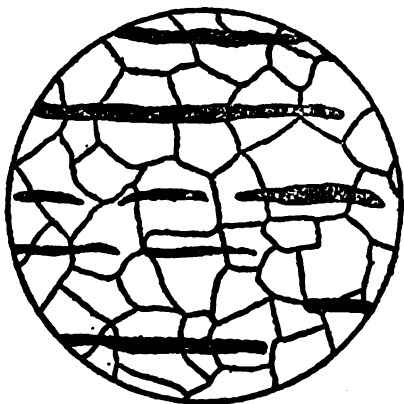


Fig. 128. — Wrought iron. Longitudinal section. Magnification not stated. (Longmuir.)



Fig. 129. — Wrought iron. Longitudinal section. Magnified 100 diameters. (Boynton in the author's laboratory.)

forging or squeezing, thus expelling a large amount of slag and firmly welding together the particles of iron. Through additional heating and forging or rolling the metallic mass is converted into such elongated shapes as blooms, billets, bars, etc. These operations so affect the structure as to impart unlike appearances to sections cut longitudinally, i.e. in the direction of forging or rolling, and sections cut transversally, i.e. at right angles to that direction. The microstructure of the longitudinal section of a wrought-iron bar is shown in Figures 128 and 129. From our knowledge of the chemical composition of wrought iron we should be able to anticipate its microstructure. The ground mass or matrix of the metal consists of polyhedral crystalline grains of iron, that is of ferrite, similar in every respect to the crystalline grains of pure iron and of pure metals in general described in Chapters IV and V. The ferrite of wrought iron, however, as explained in Chapter V, is not pure iron but rather a solid solution of iron in which are dissolved small quantities of silicon,

phosphorus and other minor impurities. This true character of commercial ferrite is too often lost sight of and the constituent considered as pure iron. The difference in coloration between adjacent grains of this commercial ferrite should be noted, and will of course be readily understood in view of the explanation given in Chapter IV to account for this phenomenon. Many irregular black lines, varying much in thickness and length, but all running in the same direction are clearly seen. These lines indicate the location of the slag which has assumed the shape of fibers or streaks running in the direction of the rolling or forging, thus imparting a fibrous *appearance* to the metal.

The presence of a small amount of carbon in wrought iron results in the occurrence of a new constituent in the shape of small dark particles located between some of the grains. Under low magnification these carbon-holding particles are not readily dis-

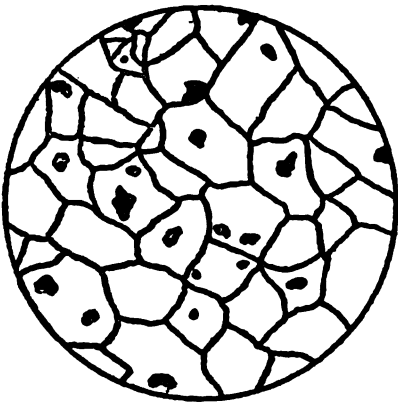


Fig. 130. — Wrought iron. Transverse section. Magnification not stated. (Longmuir.)

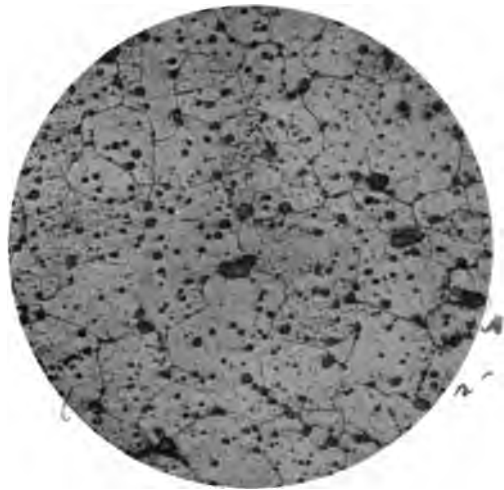


Fig. 131. — Wrought iron. Transverse section. Magnification 100 diameters. (Boylston.)

tinguishable from slag particles and as this carburized constituent is not a very important one in the case of wrought iron it seems advisable to postpone its description. Summing up, wrought iron consists essentially of a mass of ferrite containing many elongated particles of slag.

Microstructure of Transverse Section. — The microstructure of the transverse section of a wrought-iron bar is illustrated in Figures 130 and 131. Like the structure of the longitudinal section, it consists of a polygonal network, indicating that the metal is made up of polyhedral crystalline grains of ferrite. The slag, however, which in the longitudinal section occurred as fibers running in a direction parallel to the rolling or forging, here assumes the shape of irregular, dark areas, corresponding to the cross sections of the slag fibers. It will be noted that in both the longitudinal and transverse sections the ferrite grains are equi-axed, that is they show no sign of having been elongated in the direction of the rolling. It was thought for many years that wrought iron actually had a fibrous structure and, indeed, the number of persons still holding this view is surprisingly large. Many valuable properties were attrib-

uted to puddled iron on account of its "fibrous structure" which were denied to steel because of its "crystalline structure." The microscope has summarily disposed of this erroneous belief in showing that the ferrite constituting the bulk of wrought iron is in no way different from the ferrite forming the bulk of low carbon steel. Both are equally crystalline.

Structural Differences between Various Kinds of Wrought Iron. — According to W. Campbell charcoal hearth iron can sometimes be distinguished from puddled iron through the presence in the former of bands of ferrite containing more or less pearlite (the carburized constituent of steel soon to be described) especially in their centers. The occurrence of these bands is ascribed to the carburizing of the iron by the glowing charcoal during the process of manufacture. Fagoted iron also contains ferrite and pearlite bands from the steel scrap used in its production but in these the pearlite

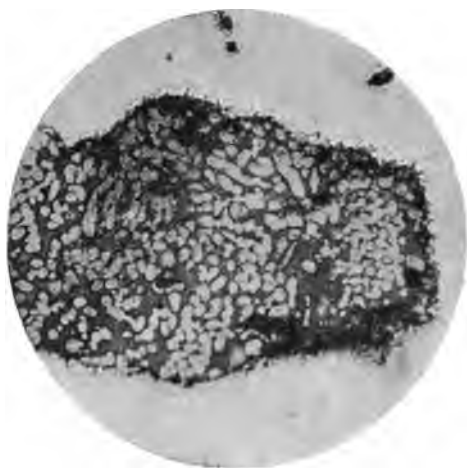


Fig. 132. — Particle of slag in wrought iron.
Magnified 200 diameters. (Guillet.)

does not decrease from center to outside, sharp lines of division existing between the bands and the ferrite matrix of the iron. It is difficult to distinguish between the structure of bushed iron and that of puddled iron on the one hand and of charcoal iron on the other; when ferrite-pearlite bands occur in bushed iron they resemble those present in charcoal iron, while in the absence of such bands the structure resembles that of puddled iron.

Chemical Composition of Slag. — The essential chemical constituents of the slag produced in the puddling furnace and retained in part by the iron are iron oxides, both ferric (Fe_2O_3) and ferrous (FeO), oxide of manganese (MnO), silica (SiO_2), and phosphoric acid (P_2O_5). Of these the oxides of iron and manganese are basic in their chemical affinity while silica and phosphoric acid are acid. These bases and acids combine with each other to form neutral compounds: silicates and phosphates of iron and manganese.

Microstructure of Slag. — When highly magnified (Fig. 132) it is found that the slag fibers are really made up of at least two constituents, a dark and a lighter one, the light constituent moreover often occurring in the form of small rounded areas.

We are naturally led to speculate as to the nature of these two distinct constituents of the slag, and in view of our knowledge of the chemical composition of slag as stated in the preceding paragraph we are tempted to conclude that one of the constituents is a silicate of iron and manganese while the other is a phosphate of the same bases. The accuracy of this deduction, however, remains to be proven.

According to Matwieff the rounded light areas consist of iron oxide mixed or not with manganese oxide, and the darker background of silicate of iron and manganese.

Matwieff recommends the following method to distinguish between the different constituents of slag. The polished sample placed in a tube is heated and treated by a current of pure hydrogen which causes the reduction of the metallic oxides while the silicates are unaffected. To detect the presence of ferrous oxide (FeO) the sample heated to a red heat is acted upon by steam, a treatment resulting in oxidizing the ferrous oxide into magnetic oxide (Fe_3O_4), while the silicates again remain unaltered. To detect the presence of manganese in the particles of oxides revealed by the hydrogen treatment the previously treated sample is repolished and etched with a dilute solution of ferric chloride in alcohol: if the white metallic grains resulting from the hydrogen treatment are colored darker than the surrounding iron they contain some manganese. Finally to detect the presence of iron and manganese sulphide the polished sample is etched with a dilute solution of tartaric acid which colors sulphide of manganese lightly and iron sulphide decidedly.

Rosenhain considers it probable that the two distinct constituents of wrought-iron slag are two different silicates or, possibly, oxides of iron.

It is seen that writers generally ignore the presence of phosphoric acid in the slag from the puddling furnace, and still it generally contains from 3 to 5 per cent of it, and occasionally considerably more. If we assume that this phosphoric acid forms with iron a phosphate of the formula $3\text{FeO} \cdot \text{P}_2\text{O}_5$, a simple calculation, according to atomic weights of the elements involved, will show that the presence of 5 per cent of phosphoric acid would mean the formation of over 12.50 per cent of this phosphate of iron. It is hardly to be supposed that this phosphate is absorbed by some other constituent of the slag. On the contrary it seems highly probable that it must be present as a distinct constituent.

Influence of Thermal and Mechanical Treatments. — The dimensions of the ferrite grains of wrought iron are affected by the treatments, both thermal and mechanical, received by the metal. The effect of these treatments upon the structure of iron and steel will be considered in another chapter.

CHAPTER VII

LOW CARBON STEEL

In this and the following chapters steel will be considered as a pure alloy of iron and carbon, i.e. free from the impurities (silicon, manganese, sulphur, and phosphorus) always present in commercial products. The influence of these elements upon the structure of steel will form the subject of another chapter.

Normal Structure. — The structures described in this and the next chapter refer to the condition of steel after forging followed by heating to, and slowly cooling from, a high temperature (900 to 1000 deg. C.). Such treatments, for reasons that will be understood later, promote soundness, remove internal strains, prevent excessive coarseness of structure (as in castings), and permit a state of stable equilibrium to be assumed by the constituents. The resulting structure may be conveniently called the “normal” structure and it will be so called in these pages.

Grading of Steel vs. Carbon Content. — Steel is generally graded according to the amount of carbon it contains. The following terms are those most commonly used:

Very low carbon steel, very mild, or extra mild steel,	
very soft or dead soft steel	carbon not over 0.10 per cent
Low carbon steel, mild steel, soft steel	carbon not over 0.25 per cent
Medium high carbon steel, half hard steel	carbon 0.26 to 0.60 per cent
High carbon steel, hard steel	carbon over 0.60 per cent
Very high carbon steel, very hard, or extra hard steel	carbon over 1.25 per cent

This classification is somewhat arbitrary as there are no sharp lines of demarcation universally recognized between the various grades.

It will be seen in another chapter that steel containing about 0.85 per cent carbon is also known as eutectoid steel, steel containing less carbon as hypo-eutectoid steel, and more highly carburized metal as hyper-eutectoid steel.

Low Carbon Steel vs. Wrought Iron. — As already mentioned the distinction between low carbon steel and wrought iron is based upon the difference between the methods employed for their respective manufacture rather than upon unlike chemical or physical properties, for these metals may indeed be quite identical both physically and chemically. The mere melting of wrought iron would undoubtedly, in accordance with the universally accepted definition of steel convert it into steel since we would now have a malleable metal *initially cast*. Such treatment would of course result in the elimination of the slag mechanically retained by the wrought iron: the melted metal would be slagless, barring cemented steel, another essential property of steel. Since wrought iron generally contains but a small amount of carbon, melting it would convert it into low carbon steel.

The Structure of Low Carbon Steel. — From the above considerations regarding the resemblance between wrought iron and low carbon steel, the structure of the latter may fairly be anticipated. Seeing that low carbon steel may be considered as wrought iron from which the mechanically held slag has been expelled through melting, we should expect the absence of slag to be the only marked difference between the structure of low carbon steel and that of wrought iron.

The microstructure of low carbon steel is illustrated in Figures 133 to 138. It will be seen (Figs. 133 to 136) to consist chiefly of a mass ferrite (carbonless iron) exhibiting the usual polyhedral crystalline grains described in preceding chapters. The ferrite present in low carbon steel is similar in every respect to the ferrite of wrought iron. At the junctions of many ferrite grains, however, some dark areas will be noted,

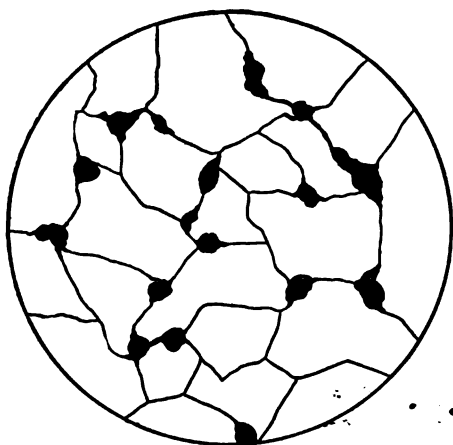


Fig. 133. — Steel. Carbon 0.08 per cent.
Magnification not stated. (Arnold.)

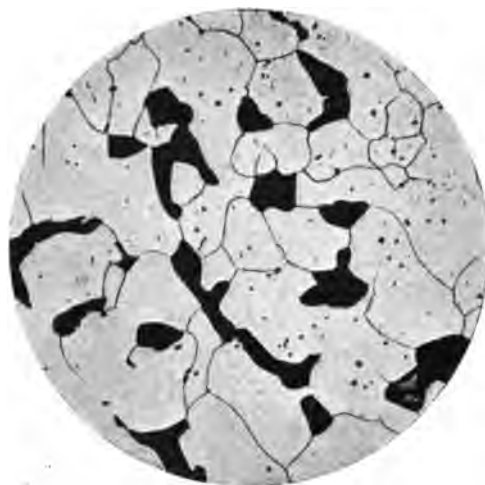


Fig. 134. — Steel. Carbon about 0.20 per cent.
Magnified 200 diameters. (Guillet.)

an evidence of the existence in the metal of another constituent. Since ferrite is practically free from carbon, it is evident that the carbon present in the steel must have segregated into these small dark masses. As to the exact nature of this dark constituent it will be apparent that it cannot consist of pure carbon, for it is well known that the carbon present in steel does not exist in the free state but on the contrary is combined with some of the iron forming a definite chemical compound or carbide of iron whose formula is Fe_3C .¹ This iron carbide must necessarily be located in the dark areas, but are these made up exclusively of this carbide? To find an answer to this question let us examine the structure of steel under a higher magnification (Figs. 137 and 138). This reveals the existence of two components in each dark particle occurring as small wavy or curved parallel plates or lamellæ alternately dark and white. As to the nature of these two components, it is evident that one of them must be the

¹ The existence of the carbide Fe_3C in unhardened steel was first shown in 1885 by Abel and Muller, working independently, and has since been confirmed by many other investigators. Its existence is proved by dissolving unhardened steel in a suitable solvent and analyzing the carbonaceous residue.

carbide Fe_3C and the other necessarily iron or ferrite, since according to the proximate analysis of steel, these are the only two constituents which, to the best of our knowledge, are present in pure unhardened carbon steel.

Pearlite. — Howe named the microscopical constituent just described pearlite (originally written pearlyte) following in this Dr. Sorby who was the first observer to describe it and who had proposed for it the name of “pearly constituent” because it frequently exhibits a display of colors very suggestive of mother-of-pearl, especially when viewed by oblique illumination. This appearance is due to the fact that these plates are extremely thin, seldom measuring over $\frac{1}{25000}$ of an inch in thickness, and that the plates of carbide, being much harder than the ferrite plates, stand in relief

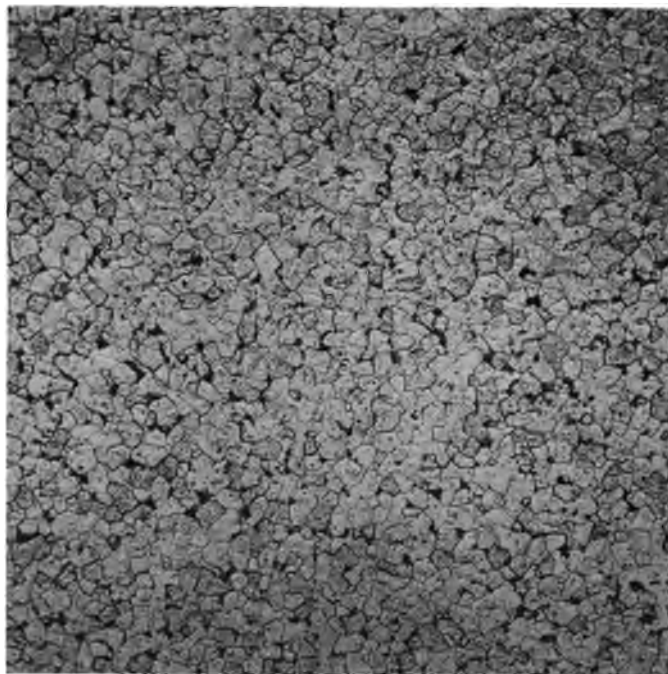


Fig. 135. — Steel. Carbon 0.08 per cent. Magnified 100 diameters. (Boylston.)

after polishing, resulting in an arrangement very similar to the refraction gratings of physicists. Mother-of-pearl likewise is made up of very thin alternate plates of different colors and possibly of different hardness. The carbide plates remain bright not being affected by the usual etching reagents, while the ferrite plates appear dark because of their being somewhat tarnished by the etching and also because, being depressed owing to their greater softness, they stand in the shadow of the carbide plates. It will be shown in another chapter that in many series of alloys of two metals the alloy of lowest melting-point called the “eutectic” alloy, nearly always exhibits a composite structure like that of pearlite, i.e. made up of parallel plates alternately of one and the other constituents. It will also be shown that in spite of this very great structural resemblance pearlite is not a true eutectic alloy. Howe proposed

to call "eutectoid" the kind of mechanical mixture found in pearlite and this most appropriate term has been universally adopted.

Because of the minute dimensions of the lamellæ of pearlite a high magnification, generally not less than 250 or 300 diameters, is required for its resolution.

It should be stated here that pearlite does not always assume such a distinctly laminated structure. In many instances its structure remains ill defined or has a granular rather than a lamellar appearance, while its behavior towards the etching reagents likewise varies. It will be shown at the proper time that this is due to the treatments to which steel may be subjected and that the exact nature of these ill-defined forms of pearlite (often called transition constituents) has given rise to a large amount of discussion and has been the object of many investigations. It may be assumed for the present that any pearlite which is not distinctly lamellar is not true pearlite.

It will be noted that in Figure 134 the pearlite occupies about twice the area covered by the same constituent in Figure 133. We infer from this that the amount of



Fig. 136. — Steel. Carbon about 0.20 per cent.
(L. T. Holt, Correspondence Course student.)

pearlite in low carbon steel at least increases progressively with the carbon content. Doubling the amount of carbon doubles of course the proportion of the iron carbide in the steel, and since the amount of pearlite is apparently also doubled it follows that iron carbide and ferrite must unite with each other in fixed ratio to form pearlite, in other words that pearlite always contains the same proportion of carbide and hence also of carbon. The accuracy of this conclusion will soon be shown.

Free Ferrite. — To distinguish between the ferrite included in pearlite and the ferrite forming the balance of low carbon steel, the latter is sometimes called "free" ferrite, "structurally free" ferrite, "excess" ferrite, "massive" ferrite, "non-eutectoid" or "pro-eutectoid" ferrite, "surplus" ferrite. In these lessons it will be referred to as free ferrite while the ferrite forming part of the pearlite will be called pearlite-ferrite. Some writers refer to the latter as eutectoid-ferrite.

In the absence of any conclusive evidence to the contrary, it is natural to infer

that free ferrite and pearlite-ferrite are identical, that is pure iron in pure steel and iron holding in solution small quantities of silicon and phosphorus, and possibly of other impurities, in impure (commercial) steel.¹

Cementite. — The name of cementite has been given by Howe to the carbide Fe_3C and universally adopted. The term is derived from “cement” steel (cementa-

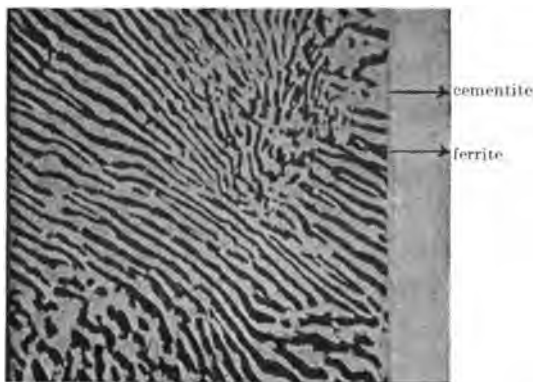


Fig. 137. — Steel. Structure of pearlite. Magnified 1000 diameters. (Osmond.)

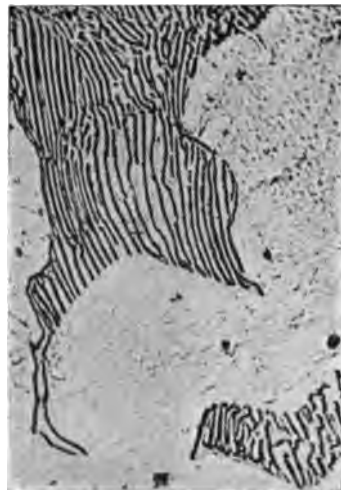


Fig. 138. — Steel. Hypo-eutectoid. Magnified 750 diameters. Pearlite particles and surrounding ferrite. (Gærens.)

tion steel, blister steel, converted steel) which being generally a high carbon steel contains a great deal of this carbide, that is of cementite.

According to the atomic weights of iron (56) and of carbon (12) cementite must contain

$$\frac{12 \times 100}{3 \times 56 + 12} = 6.67 \text{ per cent carbon}$$

The carbon present in cementite is frequently referred to as “cement” carbon, occasionally as carbide carbon, to distinguish it from other forms of carbon found in iron and steel and to be described later (hardening carbon, graphitic carbon, temper carbon, etc.).

Cementite is an extremely hard substance, being in fact the hardest of all the constituents occurring in iron and steel, harder even than hardened, high carbon steel. Howe states that it is harder than glass and nearly as brittle. As it scratches

¹ This has been doubted by some writers, however, who have noted that the ferrite of some pearlitic steels was more readily colored on etching than free ferrite and they saw in this and in some other evidences an indication that pearlite-ferrite may be less pure than free ferrite. Benedicks for instance believes, or at least believed at one time, that the pearlite-ferrite of some steels could contain as much as 0.27 per cent of carbon dissolved in beta iron, whereas free ferrite is in the alpha condition. This carburized and allotropic ferrite Benedicks called “ferronite.”

feldspar but not quartz it is generally assigned to rank 6 or 6.5 in the Mohs scale of hardness.¹

It will be shown later that when steel contains an appreciable amount of manganese, as is nearly always the case in commercial products, a portion at least of this manganese also forms a carbide Mn_3C and that this carbide unites with the iron carbide Fe_3C to form cementite. It is well to bear in mind, therefore, that in commercial steel cementite generally contains besides Fe_3C varying amounts of this carbide of manganese. As the atomic weight of manganese is nearly the same as that of iron, 55 compared to 56, it so happens that the presence of manganese in cementite affects but very little its carbon content, which for all practical purposes may be taken as 6.67 regardless of the amount of manganese it may contain. Cementite containing much manganese has been called manganiferous cementite by some writers.

Recent investigations tend to show that cementite may also contain small amounts of silicon and sulphur dissolved in it possibly as silicide and sulphide of iron respectively, although Stead and W. H. Hatfield mentioned the presence of silicon carbide. It will be shown elsewhere that some of these elements (manganese and sulphur) apparently increase the stability of cementite while silicon decreases it.

Baykoff has advanced the theory that cementite is not a definite compound or mixture of definite compounds but a solid solution.

Cementite generally remains bright and brilliant after the ordinary etching treatments employed to reveal the structure of steel. Sodium picrate, however, colors it deeply (see Chapter VIII).

¹ The Mohs scale is as follows, beginning with the softest and ending with the hardest mineral and each mineral being capable of scratching the preceding ones: (1) Talc, (2) Gypsum, (3) Calcite, (4) Fluorite, (5) Apatite, (6) Feldspar, (7) Quartz, (8) Topaz, (9) Corundum, and (10) Diamond.

CHAPTER VIII

MEDIUM HIGH AND HIGH CARBON STEEL

Medium High Carbon Steel. — The normal structure of steel (i.e. its structure after working, reheating to a high temperature and slow cooling) containing about 0.30 per cent carbon is illustrated by a drawing in Figure 139 and by a photomicrograph in Figure 140. It will be noted, on comparing this structure with that of lower carbon steels (Chapter VII), that the introduction of more carbon in the iron has resulted, as would be expected, in the occurrence of a greater amount of pearlite and of a correspondingly smaller proportion of ferrite. The pearlite occupies now roughly about one third of the total area. The junction lines between the grains of ferrite



Fig. 139. — Steel. Carbon 0.38 per cent.
Magnification not stated. (Arnold.)

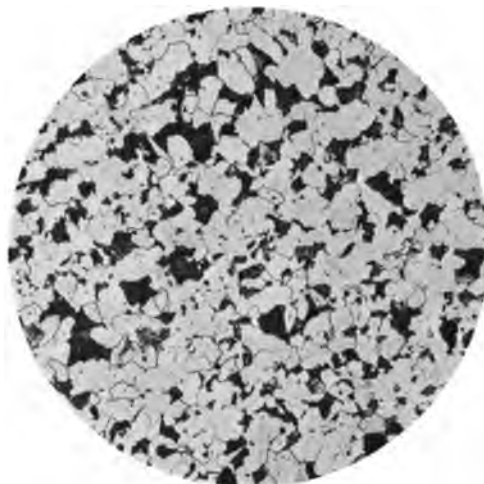


Fig. 140. — Steel. Carbon 0.30 per cent. Magnified 150 diameters. Forged and annealed. (C. C. Buck, Correspondence Course student.)

should be noted. Under sufficiently high power the pearlite areas exhibit the characteristic lamellar structure described in Chapter VII.

On further addition of carbon, the amount of pearlite, which is evidently proportional to the percentage of carbon, increases correspondingly, as shown in Figures 141 and 142 illustrating the microstructure of steel containing about 0.50 per cent carbon. The pearlite occupies here over one half of the total area. It will be noticed that the ferrite areas are only occasionally resolved into polyhedral grains, apparently because the ferrite now occurs in particles often too small to be made up of several crystalline grains. These small masses of ferrite, however, are still made up



Fig. 141. — Steel. Carbon 0.59 per cent.
Magnification not stated. (Arnold.)



Fig. 142. — Steel. Carbon 0.50 per cent.
Magnified 100 diameters. Heated to 1000
deg. C. and slowly cooled in furnace.
(Burger.)



Fig. 143. — Steel. Carbon 0.45 per cent. Magnified
1000 diameters. (Osmond.)

of crystalline matter as described and illustrated in Chapter V. A high power photomicrograph of 0.45 per cent carbon steel is shown in Figure 143. The laminations of pearlite are clearly seen.

When steel contains but a small, although appreciable, amount of ferrite, as is the case with carbon contents between 0.50 and 0.70 per cent the ferrite frequently forms envelopes or membranes surrounding the pearlite grains, an arrangement generally described as a network structure the pearlite forming the meshes and the free ferrite the net proper. These pearlite meshes are also described as "cells" or "kernels" and the ferrite membranes as "cell walls" or "shells."

It will be shown later that this network structure is promoted by rather rapid cooling from a high temperature, as for instance by cooling small pieces in air.

Structures of this type are illustrated in Figures 144 and 145. The latter illustra-



Fig. 144. — Steel. Carbon 0.50 per cent. Magnified 100 diameters. Heated to 1000 deg. C. and cooled in air. (Burger.)

tion is of special interest being a reproduction of one of Sorby's original drawings and, therefore, the first drawing of pearlite ever published.

High Carbon Steel. — Since the introduction of increasing amounts of carbon in steel results in the formation of a correspondingly increasing proportion of pearlite and decreasing proportion of ferrite, a degree of carburization must necessarily be reached, when the whole mass will be made up of pearlite, the ferrite having finally disappeared. This critical point in the structure of steel is attained when the metal contains somewhere between 0.80 and 0.90 per cent of carbon, exceptionally pure steel requiring the larger proportion of carbon and impure steel the smaller for the complete disappearance of ferrite.

Eutectoid Steel. — Steel made up exclusively of pearlite is now quite universally called "eutectoid" steel, after Howe, the name suggesting the great resemblance between pearlite and eutectic alloys while, at the same time, clearly indicating that

pearlite is not a real eutectic alloy. Previous to Howe's happy suggestion this steel was commonly described as "eutectic" or "saturated" steel. It has also been termed "aeolic" or "benmutic" steel but these names have now been abandoned. The structure of eutectoid steel is illustrated in Figures 146 and 147.



Fig. 145. — Steel. Hypo-eutectoid.
(Sorby.)



Fig. 146. — Steel. Eutectoid. Magnified
410 diameters.

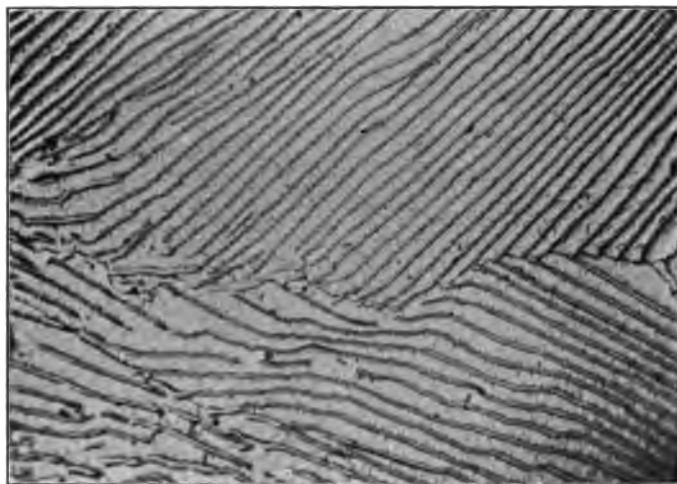


Fig. 147. — Steel. Eutectoid. Magnified 1000 diameters. (J. V. Emmons.)

Steel containing less than 0.85 per cent carbon or thereabout, and in which, therefore, some free ferrite is present, is called "hypo-eutectoid," while steel more highly carburized than eutectoid steel is called "hyper-eutectoid." It will be shown presently that hyper-eutectoid steel contains free cementite.

Hyper-Eutectoid Steel. — The normal structure of steel containing from 1.10 to 1.50 per cent carbon is illustrated in Figures 148 to 151 both under low and high

magnification. These steels will be seen to consist, like hypo-eutectoid steel, of two constituents, one of which is pearlite as clearly shown when examined under high power. The other constituent remains bright after etching and might at first be taken for ferrite. Upon reflection, however, it will be evident that such cannot be its

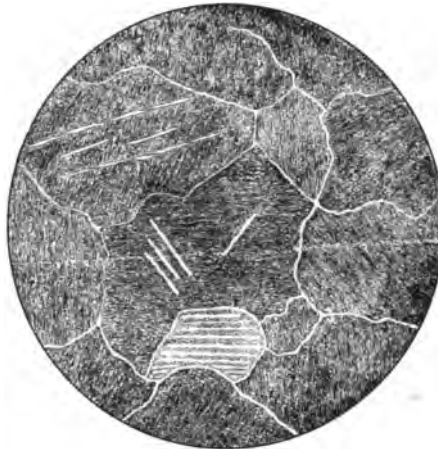


Fig. 148. — Steel. Carbon 1.20 per cent.
Magnification not stated. (Arnold.)

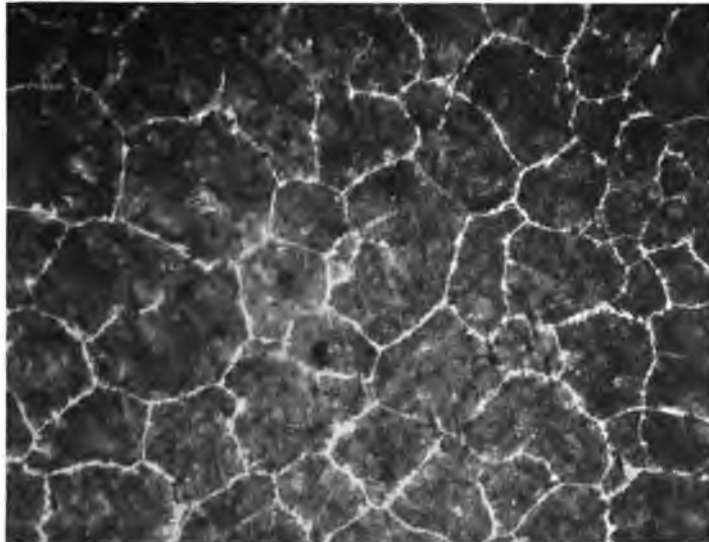


Fig. 149. — Steel. Carbon 1.10 per cent. Magnified 100 diameters.
(Boynton.)

nature. The light constituent of hyper-eutectoid steel consists of cementite which is now present in excess over the amount required to form pearlite, just as in hypo-eutectoid steel, ferrite is the excess constituent. It will be evident that the ferrite and cementite which constitute all grades of carbon steels combine with each other

in suitable proportions to form pearlite, leaving, as the case may be, an excess of ferrite (in hypo-eutectoid steel) or of cementite (in hyper-eutectoid steel). A more scientific explanation of the formation of the normal structure of steel will be offered in a subsequent chapter.

Free Cementite. — To distinguish between the cementite forming part of the pearlite (the bright plates of that constituent) and the cementite constituting the balance of hyper-eutectoid steel, the latter is generally called “free” cementite, “structurally free” cementite, “excess” cementite, “massive” cementite, “non-eutectoid” cementite, “surplus” cementite, while the cementite included in the

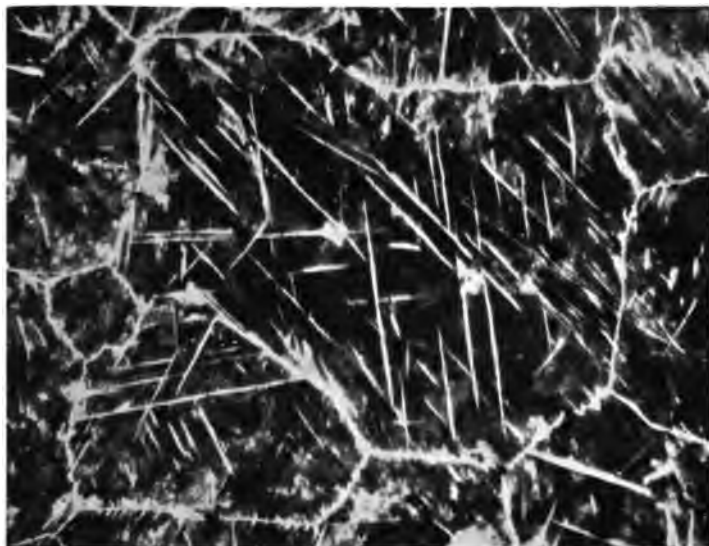


Fig. 150. — Steel. Carbon 1.43 per cent. Magnified 50 diameters.
(Boynton.)

pearlite is sometimes referred to as pearlite-cementite or eutectoid cementite. In these pages the cementite in excess over the eutectoid ratio will be called free cementite.

In the absence of any conclusive evidences to the contrary, and in conformity with the nature of eutectic alloys in general, it is assumed that free cementite and pearlite-cementite are identical in composition and properties.

As already stated in Chapter VII the cementite of commercial steel is not pure Fe_3C but contains small and varying amounts of Mn_3C , and possibly also a little silicon and sulphur.

As shown in Figures 148 and 149 hyper-eutectoid steel like hypo-eutectoid steel may assume a network structure. In both cases the meshes consist of pearlite but the net proper which in hypo-eutectoid steel represents membranes of free ferrite indicates now the occurrence of membranes of free cementite.

Hypo- vs. Hyper-Eutectoid Steel. — While there is considerable similarity between the structure of steel containing but a slight excess of ferrite and the structure of steel containing but a slight excess of cementite, a little experience and careful

examination will reveal differences in their appearances and properties which will make it possible, generally, to distinguish between them. Cementite has a more metallic luster than ferrite and remains bright and structureless, even after prolonged etching with the ordinary reagents, while ferrite is colored and, if present in sufficiently large masses, resolved into grains by such treatment. Cementite is extremely hard, standing in relief, while ferrite being soft is depressed by the polishing operation. Ferrite is readily scratched by a needle drawn across the polished surface while cementite remains unmarked. Again it will be noted that in Figures 148 and 150 some of the pearlite grains are cut by plates or needles of cementite, *independent* of the network of cementite, an occurrence seldom observed when ferrite is the excess constituent.

When cementite is in excess the pearlite grains are generally smaller and the network finer than is the case with excess of ferrite. Free cementite does not, of course,

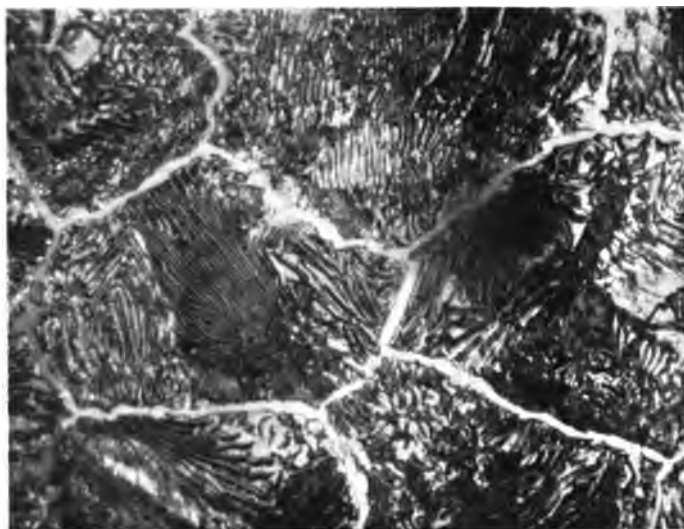


Fig. 151. — Steel. Carbon 1.43 per cent. Magnified 500 diameters.
(Boynton.)

always assume the shape of a fine network. It will be shown in subsequent chapters that its mode of occurrence depends upon the treatment to which the steel was subjected.

Etching of Cementite. — It has been seen that cementite is not acted upon by the usual reagents employed in the etching of steel sections (picric acid, nitric acid, tincture of iodine, etc.) but that it is darkly colored by a suitable treatment with sodium picrate (Chapter II) while pearlite on the contrary remains bright.

In Figures 152 and 153 is shown the structure of the same specimen of hyper-eutectoid steel etched with nitric acid (Fig. 152) and with sodium picrate (Fig. 153).

Carbon Content of Pearlite. — The percentage of carbon in pearlite and, therefore, in eutectoid steel, has been stated to be somewhere between 0.80 and 0.90 in commercial steel of ordinary quality because when steel of that degree of carburization is examined under the microscope it is found to be free from any appreciable

amount of free ferrite or of free cementite. As the presence of a very small amount of any of these two constituents in the free state, however, is very difficult to ascertain, it will be evident that it is quite impossible to speak positively as to the exact

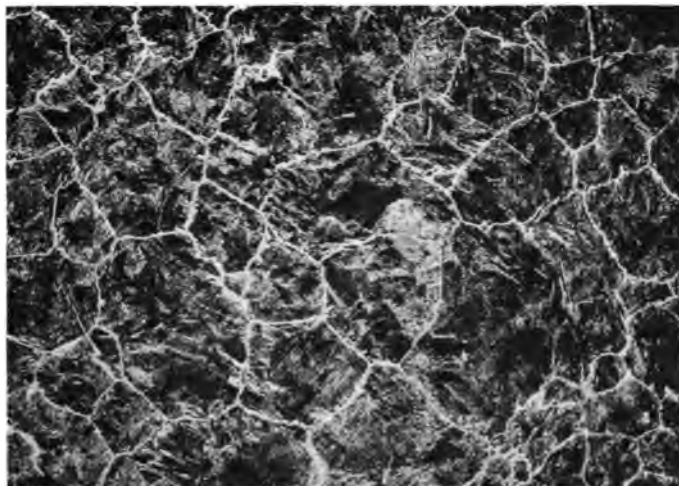


Fig. 152. — Steel. Hyper-eutectoid. Etched with nitric acid. Cementite uncolored, pearlite colored. Magnified 100 diameters. (R. W. Smyth in the author's laboratory.)

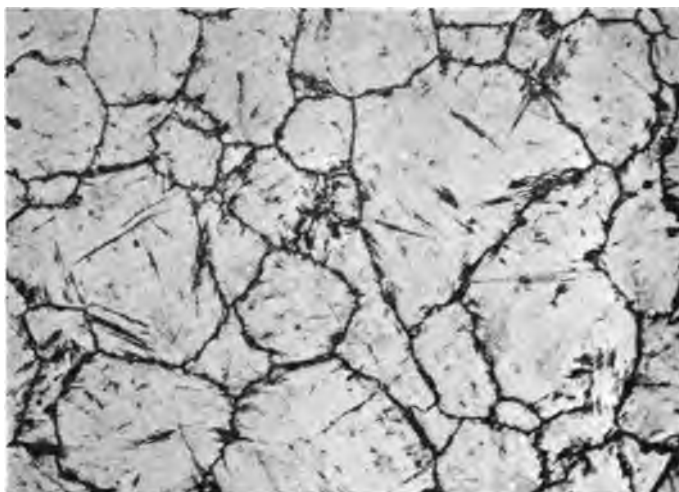


Fig. 153. — Same as Fig. 152. Etched with sodium picrate. Cementite colored dark, pearlite uncolored. (R. W. Smyth in the author's laboratory.)

amount of carbon needed to exclude both free ferrite and free cementite from the structure. Moreover this carbon content of pearlite varies somewhat with the composition of the steel and with the treatment it has received. In steel of ordinary

commercial purity the eutectoid point appears to be in the vicinity of 0.85 per cent carbon.

Structural Composition of Steel. — Bearing in mind that hypo-eutectoid steel is composed of free ferrite and pearlite and that hyper-eutectoid steel consists of free cementite and pearlite, and knowing the proportion of carbon in pearlite (0.85 per cent?) and in cementite (6.67 per cent), the structural composition of any steel may be readily calculated, provided we know the percentage of carbon it contains.

In case of hypo-eutectoid steel we have the two following equations:

$$(1) F + P = 100$$

$$(2) \frac{E}{100} P = C$$

in which F represents the percentage of free ferrite in the steel, P the percentage of pearlite, E the percentage of carbon in pearlite, and C the percentage of carbon in the steel. The first equation expresses the fact that the steel is composed of ferrite and pearlite and the second equation the fact that all the carbon in the steel is included in the pearlite. Assuming, for instance, that pearlite contains 0.85 per cent carbon and the steel 0.50 per cent carbon, the resolution of these two equations indicates that steel of that grade has the following structural composition:

$$F = \text{per cent free ferrite} = 41.18$$

$$P = \text{per cent pearlite} = 58.82$$

In case of hyper-eutectoid steel the following two equations may be written:

$$(1) P + C_m = 100$$

$$(2) \frac{E}{100} P + \frac{6.67}{100} C_m = C$$

in which P represents the percentage of pearlite, C_m the percentage of free cementite, E the percentage of carbon in pearlite, C the percentage of carbon in the steel. The first equation expresses the fact that hyper-eutectoid steel is composed of pearlite and free cementite and the second the fact that the carbon in the steel is distributed between the pearlite and the free cementite, forming E per cent of the pearlite and 6.67 per cent of the cementite. Assuming the value of E to be 0.85 and the steel to contain 1.25 per cent carbon, these equations give for a steel of that grade

$$P = \text{per cent pearlite} = 93.13$$

$$C_m = \text{per cent free cementite} = 6.87$$

Supposing that pearlite or eutectoid steel contains 0.85 per cent carbon, since the whole of that carbon is present in the cementite plates of pearlite and since cementite contains 6.67 per cent carbon (as called for by its chemical formula Fe_3C), the percentage of cementite in pearlite may be readily calculated, as follows:

$$\frac{6.67}{100} \times \text{per cent cementite} = 0.85$$

$$\text{hence, per cent cementite} = 0.85 \times \frac{100}{6.67} = 12.74$$

$$\text{and per cent ferrite} = 100 - 12.74 = 87.26$$

or roughly 1 part by weight of cementite to 6.6 parts by weight of ferrite.

If it be considered, however, (1) that the exact carbon content of pearlite is not, and hardly can be, known, (2) that it varies somewhat both with composition and treatment, and (3) that in commercial steel it is probably not far from 0.85 per cent, we are fully warranted to assume, for the sake of the great simplicity it introduces in the calculations, that pearlite contains exactly 1 part by weight of cementite to 7 parts by weight of ferrite, which would be the case if the eutectoid point corresponded to 0.834 per cent carbon, as indicated below:

1 part cementite + 7 parts ferrite yields 8 parts pearlite

or 12.50 per cent cementite + 87.50 per cent ferrite = 100 per cent pearlite

and since cementite contains 6.67 per cent carbon, 12.50 per cent cementite will contain $6.67 \times .1250 = 0.834$ per cent carbon. Assuming then that such is the carbon content of eutectoid steel, so that 1 part of cementite gives exactly 8 parts by weight of pearlite and, noting that the carbon in the steel produces exactly 15 times its own weight of cementite,¹ the calculation of the structural composition of any steel becomes extremely simple.

In case of hypo-eutectoid steel (steel containing less than 0.834 per cent carbon) we have,

$$\text{per cent total cementite} = \text{per cent total carbon} \times 15$$

$$\text{and per cent pearlite} = \text{per cent total cementite} \times 8$$

or, more simply,

$$\text{per cent pearlite} = \text{per cent carbon} \times 120$$

$$\text{i.e. } P = 120 C$$

and, of course, per cent ferrite = $F = 100 - P$.

With hyper-eutectoid steel (steel containing more than 0.834 per cent carbon) the figuring is as follows:

Since 8 parts of pearlite contain 7 parts of ferrite and since in hyper-eutectoid steel the totality of the ferrite (total ferrite) is included in the pearlite (there being no free ferrite) we have

$$\text{Total ferrite} = F = \frac{7}{8} \text{ pearlite } (P)$$

$$\text{or per cent pearlite} = P = \frac{8}{7} \text{ total ferrite}$$

$$\text{and, since total ferrite} = 100 - \text{total cementite,}$$

$$P = \frac{8}{7} (100 - \text{total cementite})$$

But total cementite = carbon $\times 15$, hence

$$P = \frac{8}{7} (100 - 15 C)$$

$$\text{or } P = \frac{800 - 120 C}{7}$$

$$\text{or approximately } P = 114 - 17 C$$

and, of course, free cementite = $C_m = 100 - P$.

Summing up, in order to find the percentage of pearlite in hypo-eutectoid steel it will suffice to multiply its carbon content by 120 ($P = 120 C$), the balance of the steel,

¹ This follows from the composition of Fe_3C indicated by the atomic weights of iron and carbon:

$$(3 \times 56) \text{ iron} + 12 \text{ carbon} = 180 \text{ Fe}_3\text{C}$$

hence, 1 part carbon produces $\frac{180}{12} = 15$ parts Fe_3C or cementite.

consisting, of course, of free ferrite ($F = 100 - P$); to find the percentage of pearlite in hyper-eutectoid steel, the percentage of carbon in the steel should be substituted for C in the formula: $P = \frac{800 - 120 C}{7}$ (or approximately $P = 114 - 17 C$) and

the balance of the steel will be made up of free cementite ($C_m = 100 - P$).

Taking, for instance, a steel containing 0.50 per cent carbon, its structural composition will be:

$$\begin{aligned} 120 \times 0.50 &= 60 \text{ per cent pearlite, and} \\ 100 - 60 &= 40 \text{ per cent ferrite.} \end{aligned}$$

If a steel contains 1.25 per cent carbon the resulting percentage of pearlite will be $\frac{800 - 120 \times 1.25}{7}$ (or more simply but less accurately $114 - 17 \times 1.25$) or re-

spectively 92.86 and 92.75 according to the formula used. The balance is free cementite.

In these pages it will be assumed for the sake of the simplicity it introduces that pearlite contains 0.834 per cent carbon, that is exactly 1 part by weight of cementite to 7 parts of ferrite.

Chemical vs. Structural Composition. — Disregarding for the present the existence of impurities, the ultimate analysis of steel reveals the presence of so much carbon and so much iron. The proximate chemical analysis of steel reveals (in steel slowly cooled from a high temperature) the presence of so much iron and so much carbide of iron, Fe_3C . In a similar way we may consider two different structural compositions, an ultimate and a proximate one. The ultimate structural composition reveals the presence of so much total ferrite and so much total cementite, while the proximate structural composition informs us of the percentages of pearlite, free ferrite, and free cementite in the steel. It will be evident that the chemical proximate composition is identical to the ultimate structural composition, the names of the constituents only being different, iron and carbide in the first case, ferrite and cementite in the latter.

These various compositions are tabulated below:

		Constituents			
Chemical Composition	ultimate	Fe	C		
	proximate	Fe	Fe_3C		
Structural Composition	ultimate	total ferrite	total cementite		
	proximate	pearlite	free ferrite	free cementite	

It is apparent that the proximate structural composition affords more valuable information than is obtainable through the other three kinds of analysis, for not only does it indicate the chemical nature of the proximate constituents but also their structural association and occurrence, upon which depend, to a very great extent, the physical properties of steel. In the following table the ultimate chemical composition as well as the structural composition, both ultimate and proximate, of steel containing from 0.1 to 2.0 per cent of carbon, have been calculated for each increase of carbon of 0.1 per cent. Corrections for variations of 0.01 per cent carbon can readily be obtained by interpolation and are indicated in a second table. The values given for the proximate compositions are based upon the assumption that pearlite contains 0.834 per cent carbon.

CHEMICAL COMPOSITION		STRUCTURAL COMPOSITION				
ULTIMATE		ULTIMATE		PROXIMATE		
C	Fe	Total Cementite	Total Ferrite	Pearlite	Free Ferrite	Free Cementite
.1	99.9	1.5	98.5	12.0	88.0	—
.2	99.8	3.0	97.0	24.0	76.0	—
.3	99.7	4.5	95.5	36.0	64.0	—
.4	99.6	6.0	94.0	48.0	52.0	—
.5	99.5	7.5	92.5	60.0	40.0	—
.6	99.4	9.0	91.0	72.0	28.0	—
.7	99.3	10.5	89.5	84.0	16.0	—
.8	99.2	12.0	88.0	96.0	4.0	—
.9	99.1	13.5	86.5	98.7	—	1.3
1.0	99.0	15.0	85.0	97.0	—	3.0
1.1	98.9	16.5	83.5	95.3	—	4.7
1.2	98.8	18.0	82.0	93.6	—	6.4
1.3	98.7	19.5	80.5	91.9	—	8.1
1.4	98.6	21.0	79.0	90.2	—	9.8
1.5	98.5	22.5	77.5	88.5	—	11.5
1.6	98.4	24.0	76.0	86.8	—	13.2
1.7	98.3	25.5	74.5	85.1	—	14.9
1.8	98.2	27.0	73.0	83.4	—	16.6
1.9	98.1	28.5	71.5	81.7	—	18.3
2.0	98.0	30.0	70.0	80.0	—	20.0

CARBON	HYP0-EUTECTOID STEEL	HYPER-EUTECTOID STEEL
%	Values to be added to % of pearlite and subtracted from % ferrite	Values to be subtracted from % pearlite and added to % cementite
0.01	1.2	0.17
0.02	2.4	0.34
0.03	3.6	0.51
0.04	4.8	0.68
0.05	6.0	0.85
0.06	7.2	1.02
0.07	8.4	1.19
0.08	9.6	1.36
0.09	10.8	1.53

These compositions are shown also diagrammatically in Figure 154 which will be readily understood. ABC represents the free ferrite in hypo-eutectoid steel, ACD the pearlite in hypo-eutectoid steel. DCEF the pearlite in hyper-eutectoid steel, DFG the free cementite in hyper-eutectoid steel, ABEH the total ferrite in any steel, AHG the total cementite in any steel, ACEH the pearlite-ferrite in any steel, and AHFD the pearlite-cementite in any steel.

Micro-Test for Determination of Carbon in Steel. — Since the amount of pearlite in steel is proportional to the percentage of carbon it contains, it should be possible to estimate the latter with a fair degree of accuracy from the area occupied by the

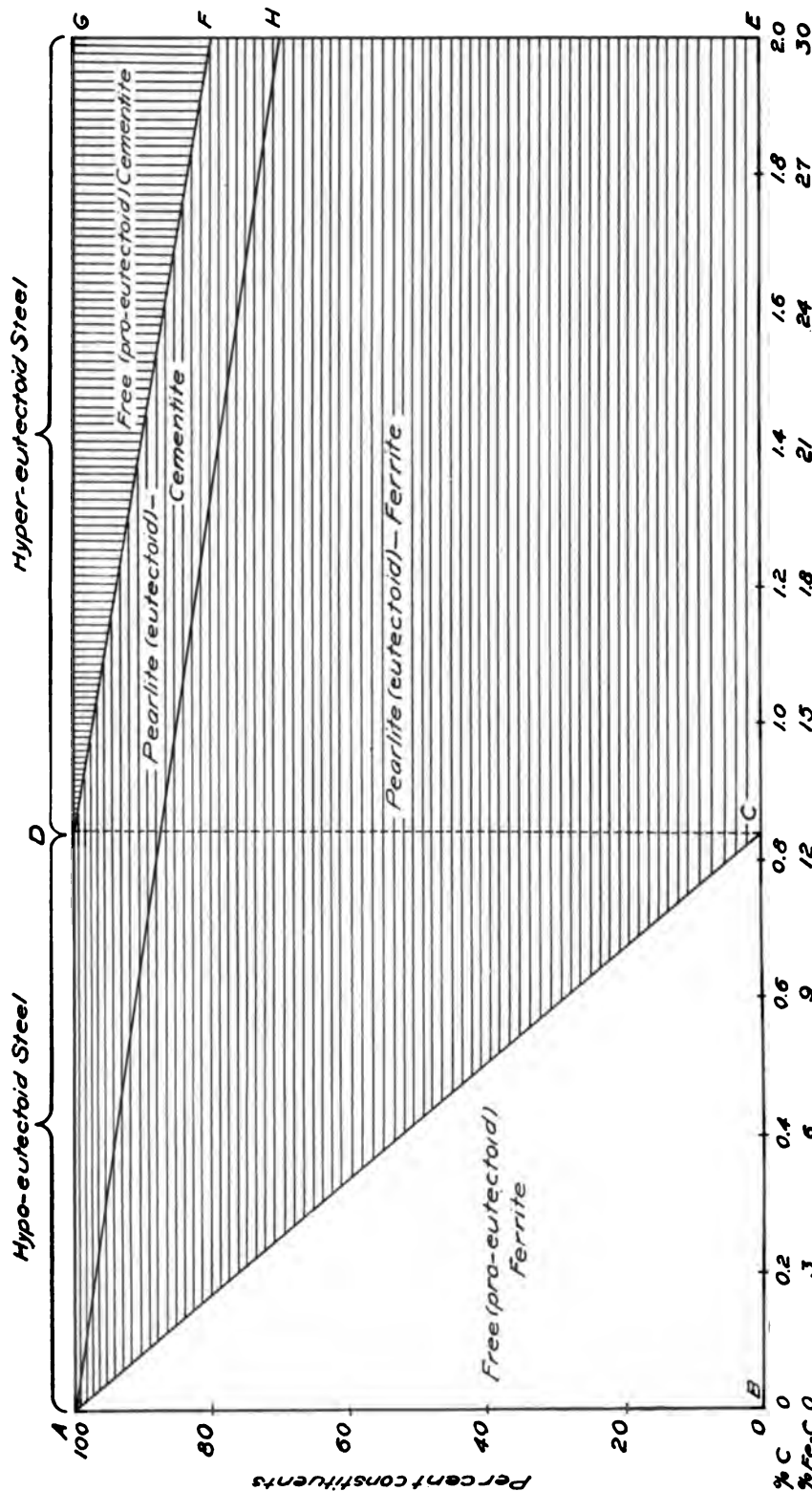


Fig. 154. — Diagram of the structural composition of slowly cooled carbon steels.

pearlite. After a little experience and by taking the necessary precautions it will be found that, in the case of decidedly hypo-eutectoid steels at least (steels containing say less than 0.60 per cent carbon), results are obtained fully as accurate as those of the colorimetric method and, on the whole, more reliable, since the possibility of serious errors is practically eliminated. By the micro-test, for instance, a steel with 0.25 per cent carbon might be reported as containing 0.20 or 0.30 per cent of that element, but it could hardly be reported as containing 0.15 or 0.35 per cent. With chemical methods on the contrary, even with the combustion method, such errors are possible, and occasionally occur, through mechanical loss, faulty manipulations, impure reagents, mistakes in weighing or figuring, etc. Chemical analysis calls for the complete destruction of the anatomy of the metal, destroying at the same time evidences of serious error; micrographic analysis, on the contrary, is based upon the anatomy itself, and therefore very serious errors are quite impossible.

In order to yield results at all satisfactory, however, care should be taken that all samples be first annealed, that is reheated to 900 or 1000 deg. C. and cooled slowly, so that the normal amounts of pearlite may be formed. To attempt to apply the micro-test to forged samples for instance is certain to lead to failure. Nor can the test be applied to hypo-eutectoid steel containing but a slight amount of free ferrite, for instance to steel with from 0.60 to 0.80 per cent carbon, because of the difficulty of estimating accurately the area occupied by so small a proportion of the constituent in excess, and therefore by the pearlite itself. In the case of hyper-eutectoid steel, the differences between the contents of free cementite in steels of materially different carbon contents is so small as to resist accurate determination. For instance, steels respectively with 1.10 and 1.40 per cent carbon will contain 95.3 and 90.2 per cent pearlite, a difference of less than 5 per cent in their contents of pearlite, a quantity too small to be estimated with satisfactory accuracy under the microscope.

To sum up, the micro-test for the determination of carbon in steel, *if it is to replace chemical determinations*, should be applied only to steels containing less than some 0.60 per cent carbon which have been annealed as above stated.

The author has found the following method to yield in some instances satisfactory results: the sample after annealing and quick polishing and etching (a few small polishing scratches will not matter) is placed under the microscope, using a 16-mm. objective and a 5X eye-piece, and its image thrown on the screen of the camera. In place of the ordinary camera screen, however, another screen is substituted of ground glass, ruled into 81 squares (9×9), so that every square covered by pearlite evidently means very nearly 0.01 per cent of carbon in the steel (exactly 0.01 per cent carbon if we assume pearlite to contain 0.81 per cent carbon). It is then sufficient to estimate the number of squares occupied by pearlite to arrive at the carbon content of the steel. The result may be checked by estimating the carbon in two or more different spots and reporting the average if the agreement is sufficiently close.

Physical Properties of the Constituents of Steel. — It will now be timely and profitable to inquire into the physical properties of the three constituents, ferrite, cementite, and pearlite of which steel in its normal condition is composed.

It will be evident that the physical properties of commercial ferrite must resemble closely those of wrought iron and of very low carbon steel. Ferrite, therefore, is very soft, very ductile, and relatively weak, having a ductility corresponding to an elongation of at least 40 per cent and a tensile strength of some 50,000 pounds per square inch. It is magnetic, has a high electric conductivity, and is deprived of

hardening power, industrially speaking at least, since carbonless iron cannot be materially hardened by rapid cooling from a high temperature.

The properties of pearlite are evidently those of eutectoid steel in its normal, i.e. pearlitic condition, from which we may infer that pearlite has a tenacity of some 125,000 pounds per square inch, an elongation of some 10 per cent, that it is hard, and for reasons later to be explained, that it possesses maximum hardening power.

With the exception of its very great hardness little is positively known as to the physical properties of cementite. It may be assumed, however, that so hard and brittle a substance must greatly lack tenacity. Its tensile strength probably does not exceed 5000 pounds per square inch and may be considerably less, while its ductility must be practically nil. It possesses no hardening power.

These properties of the constituents of steel in its normal condition are tabulated below:

CONSTITUENTS	TENSILE STRENGTH LBS. PER SQ. IN.	ELONGATION % IN 2 IN.	HARDNESS	HARDENING POWER
Ferrite	50,000 ±	40 ±	Soft	None
Pearlite	125,000 ±	10 ±	Hard	Maximum
Cementite	5000 (?)	0	Very hard	None

Tenacity of Steel vs. Its Structural Composition. — Knowing the physical properties of the three constituents of steel, it should be possible to foretell with some degree of accuracy the physical properties of any steel of known structural composition, on the reasonable assumption that these constituents impart to the steel their own physical properties in a degree proportional to the amounts in which they are present. The properties of steel made up for instance of 50 per cent ferrite and 50 per cent pearlite should be the means of the properties of ferrite and of pearlite. Let us assume such reasoning to be correct and let us apply it to the tensile strength first of hypo-eutectoid steel and then of hyper-eutectoid steel.

The tensile strength (T) of any hypo-eutectoid steel will be expressed by the following formula in terms of its structural composition, that is in terms of the percentages of ferrite (F) and pearlite (P) which it contains:

$$T = \frac{50,000 F + 125,000 P}{100}$$

in which 50,000 represents the tensile strength of ferrite and 125,000 the strength of pearlite.

Or simplifying:

$$T = 500 F + 1250 P$$

or again in terms of pearlite alone, since $F = 100 - P$

$$T = 500 (100 - P) + 1250 P$$

$$\text{or } T = 50,000 + 750 P$$

or finally in terms of carbon, since $P = 120 C$

$$T = 50,000 + 90,000 C$$

On applying this simple formula to steels containing respectively 0.10, 0.25, and 0.50 per cent carbon we find for these metals tensile strengths respectively of 59,000, 72,500, and 95,000 pounds per square inch. These values agree closely with our knowledge of the average tenacity of such steels when in a pearlitic condition, and prove the value of the formula derived from the considerations outlined above as to the relation existing between the physical properties of steel and its structural composition. It should be borne in mind that in working out this formula it has been assumed that pearlite contains 0.834 per cent carbon.

The values obtained for various hypo-eutectoid steels should be accurate only for steel in what has been termed in these chapters its normal condition, that is steel which has been worked, reheated to a high temperature, and slowly cooled. It should be noted, however, as later explained, that steel worked and finished at a fairly high temperature is practically in this so-called normal condition, so that the formula may be used, and fair results expected, to calculate the tensile strength of such hot worked steel. If the steel be worked until its temperature is quite low and, especially, if it be cold worked, it is well known that its tensile strength is generally increased. Neither can the formula be used, of course, in the case of hardened steel or of steel castings. It may, however, be applied to steel castings which have been properly annealed, when the tensile strength may be brought up to the level of steel forgings finished fairly hot as explained in another chapter.

Again the formula is of value only in case of commercial steels containing the usual proportions of impurities especially of manganese. It applies only to steels in which the percentage of manganese varies roughly with the carbon content from some 0.20 to 0.80 per cent. The presence of a larger proportion of manganese would increase the tenacity materially.

Passing to the tensile strength of hyper-eutectoid steel, our ignorance as to the tenacity of cementite does not permit the writing of a formula with the same degree of confidence. Let us assume, tentatively, however, that cementite has a tensile strength of 5000 pounds per square inch and then proceed as we did in the case of hypo-eutectoid steel.

The tensile strength of any hyper-eutectoid steel may be expressed by the following formula in terms of the percentages of pearlite (P) and cementite (Cm) which it contains:

$$T = \frac{125,000 P + 5000 C_m}{100}$$

or simplifying:

$$T = 1250 P + 50 C_m$$

or in terms of pearlite only, since $C_m = 100 - P$,

$$T = 1250 P + 50 (100 - P)$$

$$T = 5000 + 1200 P$$

or since, as previously shown, $P = \frac{800 - 120 C}{7}$

$$T = 5000 + 1200 \frac{800 - 120 C}{7}$$

or simplifying:

$$T = \frac{995,000 - 144,000 C}{7}$$

or approximately

$$T = 142,000 - 20,600 C.$$

Applying this formula to steels containing respectively 1.25 and 1.50 per cent carbon, we find for their respective strength 116,250 and 111,100 pounds per square inch, which are fair values for the average tenacity of pearlitic steels of those degrees of carburization.¹

Steel of Maximum Strength. — From the preceding considerations it seems evident that eutectoid steel must possess maximum tensile strength since the influence of the presence of ever so small an amount of free ferrite in hypo-eutectoid steel or of free cementite in hyper-eutectoid steel must necessarily be a weakening one, because of the relative weakness of free ferrite and free cementite as compared to the strength of pearlite. By most writers, on the other hand, steel of maximum tenacity is often stated to contain in the vicinity of 1 per cent carbon, that is to be slightly hyper-eutectoid.

It is not clear, however, that the results upon which the statement is based were obtained in testing steel in its *pearlitic condition*. On the contrary it seems probable that a large number of the steels tested were in a sorbitic rather than in a pearlitic condition because of relatively quick cooling through the critical range as explained in a subsequent chapter. And while it appears that pearlitic steel must have its maximum tenacity when composed entirely of pearlite, it may well be that when in a sorbitic condition maximum strength corresponds to a higher degree of carburization, i.e. 1 per cent, because sorbite may contain and indeed often does contain more carbon than pearlite. Indeed the cases on record show that when the steels were made pearlitic through very slow cooling maximum tenacity corresponds closely to the eutectoid composition. Arnold, for instance, tested a series of very pure carbon steels and after slow cooling in the furnace from 1000 deg. C. he found a very sharp maximum in the tenacity corresponding to 0.89 per cent carbon. On cooling these same steels in air, on the contrary, and therefore making them sorbitic, maximum tenacity corresponded to 1.20 per cent carbon. Harbord likewise ascertained the tenacity of very pure steels and found after slow cooling (in the furnace) from 900 deg. C that the maximum tenacity corresponded to 0.947 per cent carbon.

¹ Empirical formulas have often been suggested to express the relation between the tenacity of steel and its carbon content. Deshayes proposed for unannealed steel

$$T = 30.09 + 18.05 C + 36.11 C^2$$

Thurston (minimum values) for unannealed steel

$$T = 42.32 + 49.37 C$$

and for annealed steel

$$T = 35.27 + 42.32 C$$

Bauschinger for Bessemer steel

$$T = 43.64 (1 + C^2)$$

Weyrauch (minimum values)

$$T = 44.17 (1 + C)$$

Salom (average values)

$$T = 31.74 + 70.53 C$$

The above formulas express the tenacity in kilograms per square millimeter. Campbell, for acid open hearth steel, gives

$$T = 40,000 + 1000 C + 1000 P + xMn + R$$

and for basic open hearth steel

$$T = 41,500 + 770 C + 1000 P + yMn + R$$

in which x and y are values given in a table and dependent upon the percentage of manganese and of carbon present. R is a variable to allow for heat treatment.

Ductility of Steel vs. Its Structural Composition. — From the known ductility, as expressed by its elongation under tension, of ferrite and the known elongation of pearlite, respectively 40 and 10 per cent in two inches, it should be possible to work out a formula expressing the ductility of any hypo-eutectoid steel in the annealed (pearlitic) condition. In terms of ferrite and pearlite the ductility should be

$$D = \frac{40 F + 10 P}{100}$$

or simplifying:

$$D = .4 F + .1 P$$

or in terms of pearlite alone since $F = 100 - P$

$$D = .4 (100 - P) + .1 P = 40 - .3 P$$

and since $P = 120 C$, the ductility in terms of carbon will be

$$D = 40 - 36 C$$

Pearlitic steels for instance containing 0.25 and 0.50 per cent carbon should have elongations respectively of 31 and 22 per cent.¹

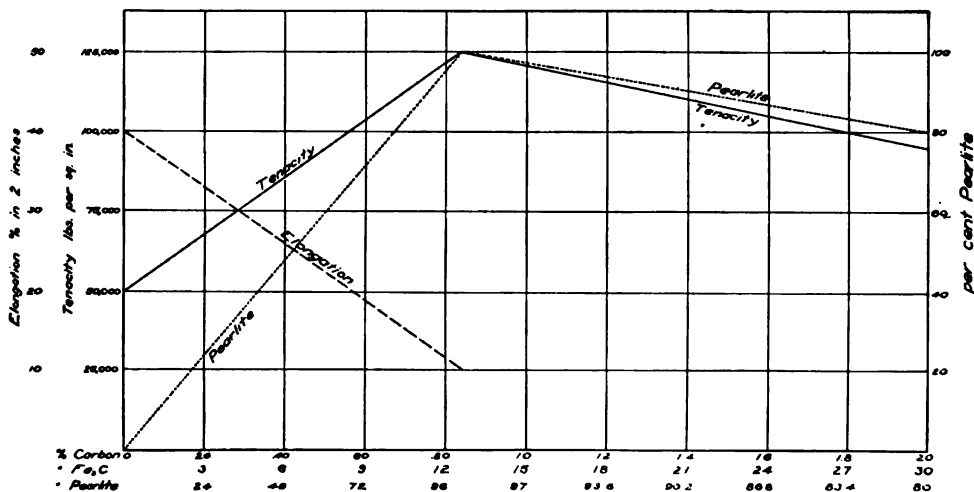


Fig. 155. — Diagram showing the relation between the tenacity and ductility of annealed (pearlitic) steels and the carbon content.

¹ It is interesting to compare this formula with some others that have been proposed. Howe gives for the elongation in 8 inches of steel under 0.50 per cent carbon

$$D = 33 - 60 (C^2 + 0.1)$$

and for steel between 0.50 and 1.00 per cent carbon:

$$D = 12 - 11.9 \sqrt[3]{C - 0.5}$$

Deshayes for the elongation in 8 inches, gives

$$D = 42 - 56 C$$

and for the elongation in 4 inches

$$D = 35 - 30 C$$

These formulas give lower values for the elongation of steel than the author's formula, but all indications point to the fact that they refer to steel in a rather sorbitic condition and, therefore, more tenacious and less ductile, whereas the formula here suggested is for truly pearlitic steel only.

Diagram Showing the Relation between the Tenacity and Ductility of Steel and Its Carbon Content. — By plotting the formulas suggested in this chapter to express the relation between the carbon content of steel and its tenacity and ductility the curves of Figure 155 are obtained. To the tenacity and ductility curves a third curve has been added showing the variation of the amount of pearlite with the carbon content.

CHAPTER IX

IMPURITIES IN STEEL

Metallic Impurities. — Commercial grades of steel always contain, besides carbon, varying amounts of silicon, phosphorus, sulphur, and manganese, often an appreciable proportion of copper and traces at least of many other metals and metalloids. These may be called the metallic impurities. Sulphur, however, is sometimes classified as a non-metallic impurity as later explained.

Non-Metallic or Oxidized Impurities. — Non-metallic or oxidized impurities, chiefly oxides, sulphides, and silicates of iron and manganese, are also frequently found in steel, principally through the retention by the metal of some of the slag produced during the refining operation. Hibbard has recently suggested the name of "sonims" for this class of impurities. They are also known as slag "enclosures" or "inclusions."

Metallic vs. Non-Metallic Impurities. — There is a sharp distinction between the behavior of metallic and non-metallic impurities, the former, with the exception of sulphur, forming true alloys with the contaminated metal, the latter being merely inclusions, their union with the metal being purely mechanical.

Gaseous Impurities. — Steel always contains some gases, apparently held in solution and called "occluded" gases, chiefly hydrogen, nitrogen, and carbon monoxide (CO).

Impurities vs. Physical Properties of Steel. — It is well known that surprisingly small proportions of some of the metallic impurities just mentioned have a very marked influence upon the physical properties of steel. Some 0.2 per cent phosphorus, for instance, renders many grades of steel so brittle as to unfit them for most commercial uses. And as it is logical to suppose that there exists a very close relation between the structure of a metal and its physical characteristics, we naturally expect to find important structural changes corresponding to marked alterations of physical properties. We should expect, for instance, the structure of a high phosphorus, brittle steel to be quite different from the structure of a low phosphorus, tough steel of otherwise identical composition. In the present state of metallography the microscope does not always reveal such differences of structures as we are led to look for. We may reasonably anticipate, however, that, as the science progresses, structural differences will be detected of a magnitude fairly in keeping with the deep changes of physical properties brought about by slight changes of chemical composition. Indeed in recent years material advance has been made in this direction and the influence of the usual impurities upon the properties of steel has been on the whole satisfactorily accounted for by metallographic methods as will be apparent from the description which follows.

Silicon in Steel. — All grades of steel contain a trace at least of silicon (Si) and occasionally as much as 0.5 per cent, and even more, most grades containing between 0.05 and 0.3 per cent.

When present in such small proportion silicon is entirely dissolved in the iron with which it forms a solid solution.¹ It is probable, however, that it is not held in solution by the iron in its elementary condition, Si, but rather as a silicide of iron, FeSi.² Since the atomic weight of iron is 56 and that of silicon 28 it will be evident that 28 parts by weight of silicon produces 56 + 28 or 84 parts by weight of FeSi, or that silicon produces exactly 3 times its own weight of FeSi $\left(\frac{84}{28} = 3\right)$. For instance

0.1 per cent silicon in the steel will give rise to the formation of 0.3 per cent of FeSi and this small amount of iron silicide will be held in solid solution by the iron. The ferrite of commercial steel, therefore, always contains a small amount of silicon in the form of an iron silicide, and let it be borne in mind that this applies to the ferrite forming part of the pearlite of all slowly cooled steels as well as to the free ferrite of hypo-eutectoid steel.

It has been stated in another chapter that when an impurity forms a solid solution with the contaminated metal, changes of crystalline forms are not generally observed. This is true in the present case, for there is apparently no structural difference between a steel with some 0.3 or 0.4 per cent silicon and a steel nearly free from that element but otherwise of identical composition. The presence of silicon in steel cannot as yet be satisfactorily detected, even qualitatively, by metallographic methods, although we have the unquestionably accurate statement of Le Chatelier that silicon causes ferrite to etch more slowly.

In view of the similarity of structure between steel containing much silicon (i.e. several tenths of 1 per cent) and steel practically free from it, we should expect that the presence of a small amount of silicon cannot affect materially the properties of steel, and this we know to be the case.

Phosphorus in Steel. — Steel of satisfactory quality contains from a trace to 0.1 per cent of phosphorus (P). As in the case of silicon this small amount of phosphorus is held in solid solution by the iron, not, however, in the elementary state, P, but as the phosphide of iron Fe₃P. The atomic weight of iron being 56, that of phosphorus 31, and the phosphide containing three atoms of iron for each atom of phosphorus, it will be obvious that 31 parts by weight of phosphorus will form $3 \times 56 + 31$ or 199 parts of the phosphide Fe₃P, or roughly, 1 part by weight of phosphorus will give rise to the formation of 6 parts of phosphide. For instance, the presence in steel of 0.05 per cent phosphorus results in the formation of 0.3 per cent of Fe₃P held in solid solution by the ferrite, this being true of the ferrite included in the pearlite of all slowly cooled steel as well as of the free ferrite of hypo-eutectoid steel.

While phosphorus in common with other metallic impurities forming solid solutions does not alter the crystalline form of steel, it is believed by some to have a marked tendency to enlarge the grains of the metal, which tendency would account for the well-known brittleness imparted to steel by phosphorus when present in ex-

¹ Some writers believe, apparently on good ground, that in cast iron at least, a metal which generally contains a considerable amount of silicon, a portion of that element crystallizes with the cementite decreasing its stability as later explained. In steel, however, the proportion of silicon present is small and if any of it dissolves in the cementite it must be in so small a quantity as to be negligible.

² Some writers mention FeSi₂ as the formula of the iron silicide present in steel but this contention is not well supported by experimental evidences.

cess of 0.1 per cent. The brittleness caused by a large grain will be considered further in another chapter.

Except for this possible enlargement of the grains, microscopical examination does not reveal the presence of the usually small percentages of phosphorus occurring in steel, unless it be segregated, although it is said by some writers that phosphorus as well as manganese causes ferrite to etch darker. The existence of portions richer in phosphorus than others may be detected by means of Stead's reagent as described in Chapter II.

Sulphur in Steel.—Steel of satisfactory commercial quality may contain from a mere trace to some 0.1 per cent sulphur, generally between 0.01 and 0.05 per cent. It is universally known that manganese and sulphur have very great reciprocal affinity so that when brought together at a high temperature they combine chemically with each other to form the sulphide of manganese, MnS . This is what happens



Fig. 156. — Manganese sulphide in steel casting. Magnified 640 diameters. (Boylston.)

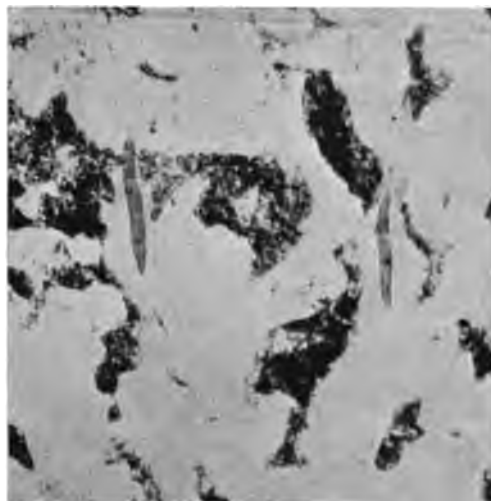


Fig. 157. — Steel. Forged. Hypo-eutectoid. Manganese sulphide in ferrite areas. Magnified 300 diameters. (Levy.)

in steel which always contains manganese as well as sulphur. From the atomic weight of manganese, 55, and that of sulphur, 32, it will be seen that 32 parts by weight of sulphur produces 87 parts of MnS , or approximately $2\frac{1}{2}$ parts of sulphide for each part of sulphur. Steel with 0.05 per cent sulphur, for instance, will contain about 0.125 per cent of MnS , provided, of course, there is enough manganese present to satisfy the sulphur which must necessarily be so in properly made steel.

The existence of the sulphide of manganese, MnS , in steel has been conclusively proven. In steel castings it occurs as rounded areas the color of which is generally described as pale or dove gray or slate color. In forgings it occurs in elongated particles, bands, or strings of the same tint, running parallel to the direction of the forging or rolling (Figs. 156 and 157).

According to Le Chatelier MnS has a melting-point superior even to that of iron, solidifying, therefore, first, and the bulk of it rising to the top of the bath or ingot, the manganese is in this way helpful in removing sulphur from steel. Some writers,

however, question this higher melting-point of MnS. Levy reports that the melting-point of pure MnS is probably not far from 1400 deg. C. and, therefore, below the melting-point of hypo-eutectoid steel at least, while the presence of some FeS would lower materially its melting-point.¹ It appears probable that the solidification of the sulphide globules must follow and not precede that of the iron.

This view seems to be supported by the location of the sulphide particles at the boundaries of the pearlite grains of eutectoid steel, in the free ferrite of hypo-eutectoid steel or in the free cementite of hyper-eutectoid steel. What MnS is retained by the solid steel, since it occurs as shown in the shape of small individual grains or elongated particles, can only injure the metal through breaking up its continuity and, in view of the very small amount of sulphur and, therefore, of MnS, present in steel of good quality, it is evident that this breaking up and its action upon the properties, must be very slight. This is in agreement with the known fact that a small amount of sulphur in steel containing also the proper amount of manganese has no appreciably injurious effect.

Seeing that steel seldom contains much more than some 0.05 per cent sulphur, hence more than 0.125 per cent MnS, it is not to be expected that this compound will always be detected in polished and etched steel sections. Indeed whenever detected it points to a segregation of the sulphide together with other impurities (ghost lines) as described later.

In case sulphur occurs in excess over the amount needed to form the sulphide MnS with the manganese present in the steel, the excess sulphur, that is the sulphur left over after satisfying the manganese, combines with some of the iron, forming the iron sulphide FeS. It should be noted at once, however, that it requires less than 2 parts by weight of manganese (atomic weight 55) to combine with 1 part of sulphur (atomic weight 32). In other words if the steel contains twice as much manganese as it does sulphur, this should theoretically be enough to convert the whole of the sulphur into the sulphide MnS. As it is very seldom indeed that steel does not contain a much larger proportion of manganese than that compared to its sulphur content, the occurrence of free FeS in steel should be very rare. It is not to be expected in metal of good quality, its presence pointing to a very abnormal composition, namely, high sulphur content and very low percentage of manganese. According to Levy, however, MnS and FeS are readily soluble in each other in the solid state, MnS being capable of holding as much as 50 per cent of FeS in solid solution. According to this writer MnS is seldom free from FeS even when the steel contains considerable manganese, the mass action exerted by the presence of so large a proportion of iron preventing the manganese from taking hold of the totality of the sulphur in spite of its greater affinity for it. MnS nearly free from FeS has a clear dove gray color free from yellowish tints, while its color becomes more yellowish as the proportion of FeS increases. Levy notes also that in high carbon steel the MnS areas are generally colored darker than in low carbon steel, indicating greater freedom from FeS, apparently owing to the fact that in high carbon steel the mass action exerted by iron is not so great since it contains less iron.

The sulphide FeS exhibits a marked tendency to form continuous envelopes or membranes surrounding each grain of pearlite (Fig. 158), and probably consisting of a

¹ Rohl reports that the freezing-point of pure MnS is 1620 deg. C. but that the compound $\text{Fe}_3\text{Mn}_2\text{S}_5$ which, in his opinion, is generally the composition of the sulphide inclusions freezes at 1365 deg. C.

eutectic alloy of iron and iron sulphide (the composition of the eutectic is apparently: FeS 85 per cent, Fe 15 per cent). These membranes being weak and brittle impart weakness and brittleness to the steel. The well-known red-shortness caused by sulphur in the absence of a sufficient amount of manganese (to form MnS) is probably due to the low melting-point (950 deg. C. according to some writers) of this iron-iron sulphide eutectic. At a high temperature the melting of this eutectic destroys the cohesion between the grains of the metal resulting in cracks being developed during the process of forging or rolling, and in extreme cases in the metal actually breaking into several pieces. The presence of a large amount of FeS in some Bessemer steel at the end of the blow, before the addition of manganese, is undoubtedly largely responsible for the marked red-shortness of the metal at this stage of the operation.

Under the microscope FeS appears yellow or pale brown.

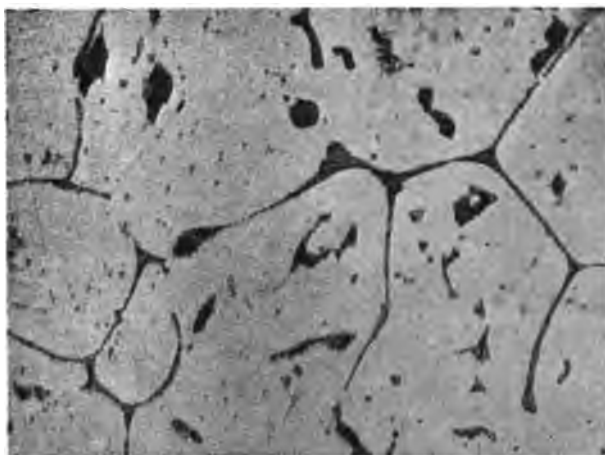


Fig. 158. — Red-short steel. Magnified 300 diameters. Sulphur 0.54 per cent. Unetched. Network of FeS. (Ziegler.)

The following is quoted from Stead: "The researches of Rohl have demonstrated beyond doubt that ferrous and manganese sulphides crystallize together in the proportions of 60 per cent FeS and 40 per cent $\text{MnS} = \text{Fe}_3\text{Mn}_2\text{S}_5$ and in mixtures containing increasing quantities of manganese sulphide up to 100 per cent, forming homogeneous isomorphous compounds of $\text{Fe}_3\text{Mn}_2\text{S}_5$ all of which under the microscope have the same appearance. Levy and Law, however, state that the homogeneous substance which contains the most FeS is lighter in color than that containing less.

When the FeS exceeds 60 per cent in the mixture a eutectic consisting of 7 per cent MnS and 93 per cent FeS appears, having a freezing point of 1181 deg. C.

When iron in excess is present in addition to an excess of FeS over the mixture $\text{Fe}_3\text{Mn}_2\text{S}_5$, a ternary eutectic is formed freezing at 980 deg. Rohl found the freezing point of pure MnS to be 1620 deg., or about 120 deg. higher than that of pure iron, and the freezing point of the compound $\text{Fe}_3\text{Mn}_2\text{S}_5$, 1365 deg.

Judging from these most valuable researches, it may be accepted beyond any doubt that when iron sulphide, and what appears to be manganese sulphide, are found associated together in the same sulphide inclusions what looks like MnS is not that compound but is $\text{Fe}_3\text{Mn}_2\text{S}_5$."

It has been contended by some that a portion of the sulphur present in steel and cast iron is dissolved in the cementite and that its presence increases the stability of that constituent. It seems probable, however, in view of the very small amount of sulphur generally present in steel and of the relatively large amount of manganese

that this possible contamination of cementite by sulphur, if it occurs at all, may be neglected. This has been done in the present chapter, it having been assumed that the totality of the sulphur is present as MnS or as MnS and FeS in the form of mechanical inclusions.

Sulphur Printing. — As explained in Chapter II the presence of sulphur in steel and iron, especially when segregated, may sometimes be detected by the taking of so-called "sulphur prints."

Manganese in Steel. — It has been seen that manganese combines readily with sulphur and that the resulting manganese sulphide, MnS , either alone or combined with some FeS , can be detected in polished steel sections as a pale or dove gray constituent assuming the shape of rounded areas in castings and of bands or threads in forgings. Manganese silicate is also occasionally found in steel as later explained and may sometimes be mistaken for MnS . Satisfactory tests for the distinction of these two constituents will be described.

When manganese occurs in excess over the amount required to form MnS with the totality of the sulphur present, as is almost universally the case, the manganese in excess combines with some of the carbon to form the carbide of manganese, Mn_3C , and this carbide is found associated with the iron carbide, Fe_3C , in cementite. The cementite of commercial steel, therefore, is seldom a pure iron carbide, containing on the contrary varying amounts of Mn_3C . Since iron and manganese have practically the same atomic weight, however (55 and 56 respectively), it remains practically true that carbon forms 15 times its own weight of cementite, even when the latter contains a large proportion of Mn_3C .

There is no metallographic test by which cementite free from manganese can be distinguished from cementite rich in Mn_3C .

Some authors mention the possible presence of the manganese silicide, MnSi , in steel, while solid solution between manganese and iron is frequently referred to. While manganese and iron (ferrite) undoubtedly form solid solutions, it does not seem likely that these are produced when manganese is present in small proportion, say not over 1 per cent. In that case it seems more probable that manganese is found in the two forms described above, (1) as a manganese sulphide MnS , containing practically the totality of the sulphur in steel of good quality, that is, containing not over 0.05 per cent sulphur and not less than 0.25 per cent manganese and (2) as the manganese carbide Mn_3C , associated with Fe_3C in cementite.

Chemical vs. Structural Composition. — Knowing the probable chemical forms of the five metallic impurities always present in steel, carbon, silicon, phosphorus, sulphur, and manganese, as well as their structural associations, it will be interesting and profitable to consider accordingly the proximate chemical composition as well as the ultimate and proximate structural compositions of a steel of known ultimate chemical composition. Let us assume a steel of the following ultimate chemical composition:

C	0.50 per cent
Mn	0.80 " "
S	0.05 " "
P	0.04 " "
Si	0.10 " "
Fe (by diff.)	98.51 " "
	<hr/> 100.00

Bearing in mind the atomic weights of these elements (Fe, 56; C, 12; Mn, 55; S, 32; P, 31; Si, 28) and the formulas of the chemical compounds formed (MnS , FeSi , Fe_3P , Mn_3C , Fe_3C), it will be readily seen that:

- (1) 0.05 per cent S will give rise to the formation of 0.13 per cent MnS .
- (2) 0.13 per cent MnS contains about 0.08 per cent Mn.
- (3) This leaves $0.80 - 0.08 = 0.72$ per cent manganese in excess to combine with C.
- (4) 0.72 per cent Mn will form 0.77 per cent Mn_3C .
- (5) 0.77 per cent Mn_3C contains about 0.05 per cent carbon.
- (6) This leaves $0.50 - 0.05 = 0.45$ carbon to combine with iron.
- (7) 0.45 per cent carbon results in the formation of 6.75 per cent of Fe_3C .
- (8) 0.04 per cent of P corresponds to about 0.25 per cent of Fe_3P .
- (9) 0.10 per cent Si gives 0.30 per cent FeSi .

The proximate chemical composition of the steel considered will be

Fe_3C	6.75 per cent
Mn_3C	0.77 " "
Fe_3P	0.25 " "
FeSi	0.30 " "
MnS	0.13 " "
Fe (by diff.)	91.80 " "
	<hr/> 100.00

As to the ultimate structural composition of the steel, we know that the cementite contains the Fe_3C and the Mn_3C hence we have $6.75 + 0.77 = 7.52$ per cent cementite. In pure steel the percentage of cementite would have been $0.50 \times 15 = 7.50$ per cent. The slight difference between the two numbers is due to the presence of manganese in the commercial steel, and to a slight difference between the atomic weights of manganese and that of iron (55 compared to 56), a difference so slight that for all practical purposes we may assume that in commercial steels as well as in pure steel the percentage of carbon multiplied by 15 gives the amount of cementite formed. The total ferrite present in this steel contains all the free iron, as well as the small proportions of Fe_3P and FeSi present, hence this steel contains $91.80 + 0.25 + 0.30 = 92.35$ total ferrite. In pure steel the proportion of total ferrite would have been $100 - 7.50$ or 92.50 per cent. The difference between the two values is evidently due to the presence of a trifle greater amount of cementite, and to the presence of 0.13 per cent MnS .

The ultimate structural composition of the steel under consideration is, therefore:

Total ferrite	92.35
Cementite	7.52
MnS	0.13
	<hr/> 100.00

Finally its proximate structural composition will be, since the pearlite of hypoeutectoid steel contains 8 times the weight of total cementite (assuming the eutectoid carbon point to be 0.834 per cent):

Pearlite	$7.52 \times 8 = 60.16$
Free ferrite (by diff.)	39.71
MnS	.13
	<hr/> 100.00

Ignoring the presence of impurities the quick method described in Chapter VIII would have given pearlite 60 per cent, ferrite 40 per cent, i.e. values which may be considered identical for any practical purposes. It follows from this that in calculating the structural composition of any carbon steel of ordinary commercial quality the presence of the impurities need not be considered; the steel may be treated as if it were made exclusively of iron and carbon.

The relation between chemical and structural compositions, both ultimate and proximate, is further shown in the following table:

CHEMICAL COMPOSITION		STRUCTURAL COMPOSITION			
ULTIMATE	PROXIMATE	ULTIMATE	PROXIMATE		
%	%	%	% Free Ferrite		
Fe(by diff.) 98.51	Fe(by diff.) 91.80	Total Ferrite 92.35	39.71 Free Ferrite		
Si 0.10	FeSi 0.30		60.16% Pearlite		
P 0.04	Fe ₃ P 0.25	Cementite 7.52	52.64 Pearlite Ferrite		
C 0.50	Fe ₃ C 6.75		0.13		
Mn 0.80	Mn ₃ C 0.77	MnS 0.13	0.13		
S 0.05	MnS 0.13				
100.00	100.00	100.00	100.00		

Non-Metallic or Oxidized Impurities. — As already mentioned steel generally contains varying amounts of non-metallic, oxidized impurities frequently called slag "enclosures," or "inclusions," while Hibbard proposed for them the name of "sonim," in which "so" stands for solid, "n" for non-metallic and "im" for impurities. They consist chiefly of iron and manganese oxides and silicate although the sulphides of iron and manganese are generally considered also as slag enclosures. These impurities are derived mainly (1) from the retention by the metal of minute particles of the slag formed during the process of manufacture, (2) from small pieces of refractory materials detached from the linings of furnaces and ladles, and (3) from the reaction-products resulting from the introduction of recarburizers or other additions.

According to Hibbard the formation of slag enclosures is due almost entirely to the "washing" action of the additions, principally of manganese, in combining with the dissolved oxides, sulphides, and silicates which are present in the steel at the end of the melting process before the manganese is added since enclosures rich in manganese must necessarily have formed after the addition of that constituent. Stead on the other hand expresses the belief that the silicate enclosures at all events are due to oxidation of manganese and silicon occurring during the passage of the molten steel through the air in passing from the ladle into the molds. In the case of iron oxide it seems probable that minute particles of it remain in suspension in the molten steel forming as many minute inclusions after solidification, while another portion, dissolved in the liquid metal, is in part precipitated during solidification.

In Rosenhain's opinion it is not proven that the sulphides and silicates are not soluble in molten steel.

After solidification the association between the slag enclosures and the steel remains a purely mechanical one; they commonly occur as rounded or elongated particles embedded in the metal.

MnS can generally be readily distinguished from other inclusions because of its characteristic dove gray color, its globular shape in castings (Fig. 156) and, owing to its plasticity, the ease with which it is elongated in forgings (Fig. 157). It seems reasonable to assume that the paler its color the greater its purity, and that a yellowish tint points to the presence of some FeS. Pure FeS, a very rare constituent of steel, has a decidedly yellow color and is more brittle. MnS generally occurs in the free ferrite of hypo-eutectoid steel, between the pearlite grains of eutectoid steel or in the free cementite of hyper-eutectoid steel.

Silicates are decidedly darker than MnS (Figs. 159 and 160) which affords a means of distinguishing between them even when they are associated in the same particles as it sometimes happens (Fig. 159). Silicates because of their relative brittleness are



Fig. 159. — Manganese sulphide (light constituent) and manganese silicate in steel. Magnified 1000 diameters. (Law.)

frequently broken and torn by the forging operation (Fig. 160). Sometimes the manganese sulphide forms dendrites embedded in a silicate matrix.

Stead recommends the placing of a drop of sulphuric acid on the polished specimen, when H_2S gas will be evolved where MnS is present, particles of silicates of manganese, on the contrary, evolving no gas. The dissolving of MnS also leaves pits. Stead also advises heat tinting as the best means of distinguishing between the sulphide and the silicate, the heating to be continued until the specimen has assumed a light brown coloration, when the MnS remaining bright can be sharply differentiated from the silicate.

No very satisfactory metallographic tests have so far been found to distinguish between oxides and silicates or between iron silicate and manganese silicate. Matwieff's attempts in that direction have been described in Chapter VI.

They are summed up by Rosenhain as follows: "According to their behavior under these reagents (hydrogen and superheated steam), the enclosures may be divided into three groups or classes:

“A. Stable bodies which are not acted upon either by hydrogen at 300° C., by superheated steam, or by weak organic acids. These are the silicates of iron and manganese.

“B. Bodies which are reduced to the metallic state by the action of hydrogen at 300° C. and are acted upon by steam but are unaffected by weak organic acids. These



Fig. 160. — Manganese sulphide (light constituent) and iron silicate in mild steel. Unetched. Magnified 1000 diameters. (Law.)

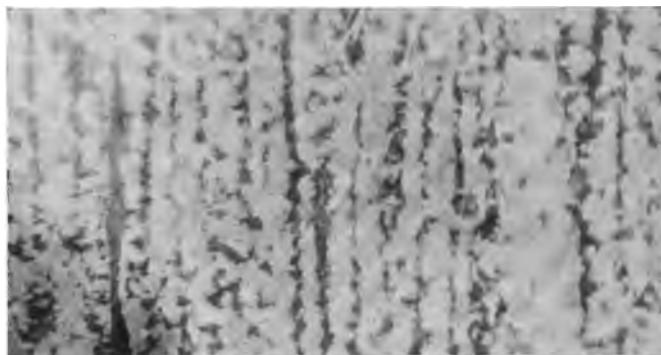


Fig. 161. — Ghost lines in low carbon steel. Magnified 95 diameters. (Boylston.)

are the oxides of iron and manganese. Oxide of manganese is not reduced by hydrogen when by itself, but in the presence of iron oxide reduction of both metals takes place. On re-polishing a sample after heating in hydrogen, the regions previously occupied by oxides appear as bright metal, like the ferrite of the surrounding iron or steel, but the presence of manganese may be detected by etching with very dilute

alcoholic solution of ferric chloride. Iron free from manganese is only very slightly colored, but if manganese is present, the reagent produces rapid coloration.

“C. Not affected by hydrogen or steam, but attacked by weak organic acids (such as tartaric acid). These are the sulphides of iron and manganese; the former is rapidly colored by this acid while sulphide of manganese is only slowly attacked. The behavior of the sulphides which are mixtures or solid solutions of the iron and manganese sulphides is not considered by Matwieff, but in the light of the work of Levy these mixed sulphides require particular study from this point of view.”

Rosenhain rightly adds that the use of gaseous reagents at moderately high temperatures is a somewhat cumbrous manipulation, particularly because, if general tarnishing of the polished specimens is to be avoided, the hydrogen must be specially



Fig. 162. — Ghost lines in low carbon steel. Magnified 2000 diameters. Manganese sulphide and pearlite particles. (Law.)

purified. It is to be hoped, therefore, that future research may yet find simpler means of identifying these substances.

At the end of the refining operation by which steel is produced, especially towards the latter part of the Bessemer blow, a considerable amount of iron oxide is formed and in spite of the steps taken for removing it from the bath (addition of manganese, etc.) some of it, occasionally quite a little, is retained by the metal, when it is a source of red-shortness, besides having other detrimental effects. This iron oxide generally occurs as small dark points visible in the polished section before etching.

Segregation of Impurities. — Ghosts. — The very small proportions of impurities generally found in steel of good quality have little, if any, injurious effect upon its most important and useful physical properties, so long as they remain uniformly distributed throughout the metallic mass, i.e. so long as the steel is chemically homogeneous. These impurities, on the contrary, may become extremely injurious when they show a tendency to “segregate,” i.e. to collect in certain portion or portions of steel castings and forgings, when the segregated portions may contain so large an

amount of impurities as to have their useful properties utterly destroyed. Segregated metal is generally brittle, weak, and hard.

Under the microscope a metal suffering from this segregation of impurities generally is found to contain bands of varying widths and lengths, technically known as

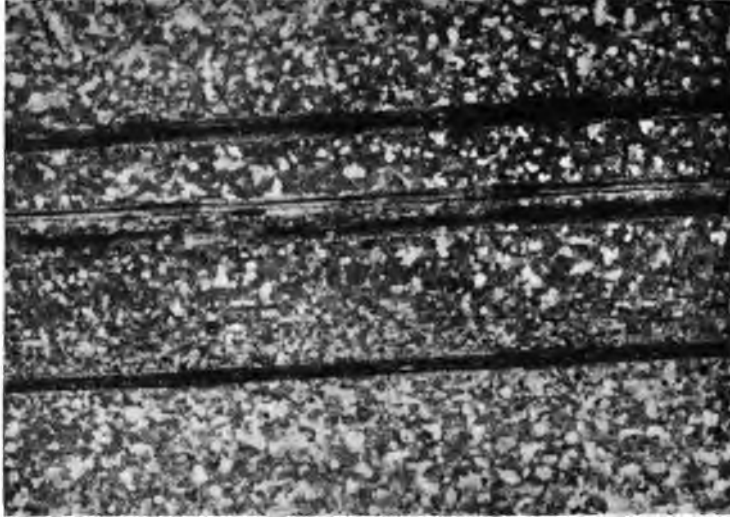


Fig. 163. — Ghost lines in low carbon steel. Magnified 10 diameters. (Law.)



Fig. 164. — Ghost lines in low carbon steel. Magnified 200 diameters. (Law.)

“ghosts” or “ghost lines,” in which the presence of abnormally large proportions of MnS and phosphorus can generally be detected by the ordinary metallographic tests. Photomicrographs of ghost lines are shown in Figures 161 to 167. Ghost lines etch more rapidly than the surrounding metal therefore appearing darker after etching even

to the naked eye. These lines can generally be detected before etching because of the manganese sulphide which they contain.

Stead describes "ghost lines" as lines of ferrite in which are embedded lenticular particles of drawn-out sulphide inclusions and he adds that when manganese sulphide is found segregated it may be taken for granted that phosphorus also is segregated in the same regions. He believes that the white ferrite lines sometimes observed in forgings are due to phosphorus segregation, the presence of that element having expelled the carbon on slow cooling. He writes that the higher the phosphorus in the steel the thicker and more pronounced are these white carbonless lines in forged

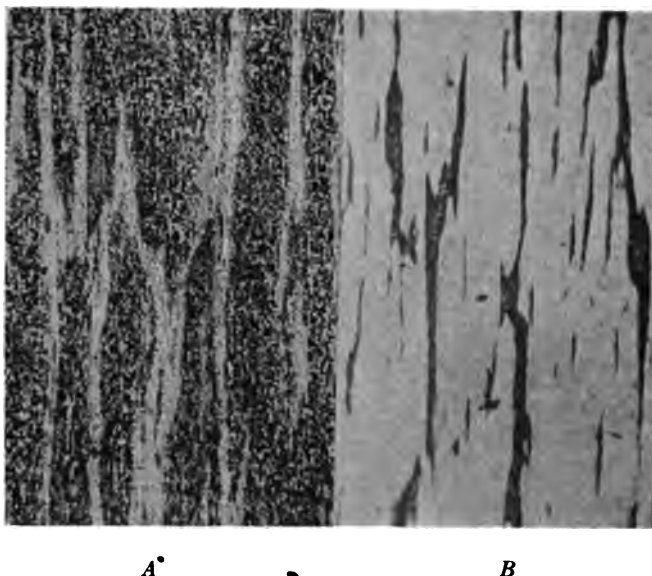


Fig. 165. — Forged steel containing about 0.3 per cent carbon and 0.3 per cent phosphorus.

A. Polished and etched in the ordinary way.

B. Heat-tinted until the phospho-ferrite bands are oxidized to a brown tint. (Stead.)

steels. In Figure 165 Stead shows the effect of heat-tinting specimens exhibiting these ferrite bands.

Stead's cupric reagent (Chapter II) is also very effective in revealing the existence of ferrite bands rich in phosphorus. The lighter portions contain the most phosphorus, copper being precipitated on the portions freer from that element.

Rosenhain and Haughton likewise bring out clearly the banded structure of certain steels by the electro-chemical deposition of copper from a solution of ferric chloride and hydrochloric acid containing a small amount of copper chloride. This reagent, Rosenhain writes, develops the banded structure of steel containing phosphorus in a striking manner, as illustrated in Figure 166. Figure 167 shows another typical instance of a banded structure.

Rosenhain accepting Ziegler's view that the particles of slag enclosures act as so many nuclei for the crystallization of ferrite in hypo-eutectoid steel and of cementite

in hyper-eutectoid steel argues that the "banded" structure of some forged steels may be accounted for through the crystallizing of ferrite around strings of enclosures formed by the rolling operation. He writes: "Again we commonly find in commercial steel a banded arrangement of ferrite and pearlite, such as that shown in Figure 167 and although this is obviously traceable to the rolling process which the steel has undergone, the banded structure is extremely persistent in spite of repeated annealing. If we consider that the enclosures present in the steel have been rolled out into long lines, and that each time the steel cools down through A_r , the ferrite tends to deposit upon these lines of enclosures, the persistent recurrence of these bands is explained. Heat treatment could, in that case, only destroy these bands if time enough were allowed for the gradual migration of the enclosures at a high tempera-



Fig. 166. — Banded structure in steel containing phosphorus. (Rosenhain.)



Fig. 167. — Banded structure in steel. Magnified 100 diameters. (L. T. Holt, Correspondence Course student.)

ture — and very prolonged annealing does break up the banded structure. The occurrence and persistence of the comparatively wide carbonless bands, studded with enclosures, which are sometimes termed 'ghosts' may be accounted for in a similar way by the original rolling out into a long band of an austenite boundary containing a comparatively large mass of enclosure."

Rosenhain would account as follows for the persistence of ferrite bands rich in phosphorus: "In the case of steel, phosphorus occurs typically in this way, being present in solid solution in the ferrite of the ingot, but in the form of solid-solution cores, so that the phosphorus content of each crystal increases from its center to its periphery. When rolled out, these crystal cores assume the form of elongated masses, and although the ferrite itself undergoes complete re-crystallization, possibly repeatedly, there is nothing to cause the phosphorus to migrate except the process of diffusion, which is particularly slow in that case. The result is that in the finished material the phosphorus-rich ferrite still remains in long bands or streaks, and these

bands pass indifferently through numbers of individual crystals — indeed, an individual crystal may lie partly within and partly outside one of these bands — the growing ferrite crystal has simply used the material it found at hand, whether rich in phosphorus or not.”

Gaseous Impurities. — It has not been possible so far to detect the presence of occluded gases in steel by means of metallographic methods. While the problem seems a very difficult one to solve, the statement that it can never be solved would not be justified, for the discovery of some metallographic treatment by which a metal rich in certain gases may be distinguished from a similar metal free from them is well within the limits of reasonable expectation.

CHAPTER X

THE THERMAL CRITICAL POINTS OF STEEL

THEIR OCCURRENCE

The structure of steel described in the preceding chapter, i.e. its normal structure, is greatly affected by the treatment or treatments, both mechanical and thermal, to which the metal may be subjected during the process of manufacture of finished objects. It is to the close relation existing between the treatment and the structure on the one hand, and between the structure and the physical properties of the metal on the other, that metallography owes its industrial importance. It is essential, therefore, that the student should have a clear understanding of these relations. As a preparation to this important study, however, it will be necessary to describe a phenomenon of the greatest moment in the treatment of steel, namely, the occurrence of spontaneous absorptions or evolutions of heat during the heating or cooling of the metal. These are generally termed the "thermal" critical points or simply "critical points," also "retardations," "transformation" points, and "critical temperatures."

Point of Recalescence. — If a piece of steel containing some 0.60 per cent carbon be heated to a high temperature, say to 1000 deg. C., and allowed to cool slowly from that temperature, and if its rate of cooling be carefully ascertained, conveniently by means of a Le Chatelier pyrometer, it is found that the cooling proceeds at first at a nearly uniformly retarded rate. If, for instance, it requires 10 seconds for the metal to cool through the first five degrees (from 1000 to 995 deg.), and 12 seconds to cool through the next five degrees (995 to 990 deg.), it will require some 14 seconds for the next five degrees, 16 seconds for the following five, and so on, the cooling through each range of five degrees being a little slower than the preceding cooling of five degrees. All cooling bodies, whatever their nature, generally follow this law. The plotting of time and temperature as coordinates yields smooth curves, sometimes approaching straight lines (see curve B, Fig. 177).

In the case of the steel we are now considering, when a certain temperature is reached, in the majority of cases some 675 to 725 deg. C., a most interesting and significant phenomenon takes place; the cooling of the metal is momentarily arrested, the pyrometer, for a certain length of time, failing to record any further fall of temperature. Indeed, when the circumstances are favorable, the temperature of the cooling mass actually rises; the metal becomes visibly hotter; it "recalcesces," hence the name of "recalcescence" given to this thermal critical point. If the experiment be conducted in a dark room, this recalcescence or spontaneous glow of the steel is plainly visible. After a while the metal resumes its normal rate of cooling which is then continued down to atmospheric temperature.

It is evident that at this critical point the surrounding atmosphere does not cease

to abstract heat from the piece of steel and, since its temperature nevertheless remains stationary or even rises, it must be that heat is here spontaneously generated within the metal in amount sufficient to make up, or more than make up, for the heat lost by radiation and conductivity.

In heating, as might be expected, the reverse phenomenon takes place: an *absorption* of heat causing a retardation in the *rise* of the temperature, or even a momentary stop, the pyrometer failing for a few moments to record any further increase of temperature or recording only an abnormally low increase, although heat continues to be applied to the steel at the same speed. Actual *lowering* of the temperature of the steel is not generally observed at this critical point on heating, i.e. the steel does not grow perceptibly colder.

Notation. — Osmond, who was the first to determine accurately the position and magnitude of the point of recalescence and who is the discoverer of the upper critical points soon to be described, adopted Tschernoff's previous notations, and designated the critical points by the letter A.¹ To distinguish critical points on cooling from those occurring on heating the former are called Ar (from the French *refroidissement*, meaning cooling) and the latter Ac (from the French *chauffage*, heating). To distinguish further between the point of recalescence and its reversal on heating on the one hand, and critical points occurring at higher temperatures on the other, the notations Ar₁ and Ac₁ are used for the recalescence point and its reversal, and Ar₂, Ac₂, Ar₃, Ac₃, for the two upper reversible critical points soon to be described. The notations, A₁, A₂, A₃, are frequently used when the points and their reversals are considered collectively. By the notation A₁, for instance, is meant the point of recalescence Ar₁ and its reversal Ac₁. These notations will be used in these chapters.

Brinell, in his important work on the heat treatment of steel, used the letter V for the point of recalescence and W for its reversal on heating. These symbols, however, are now very seldom used.

The expression "point of recalescence" is frequently used indifferently for the point on cooling, where heat is evolved causing a recalescence of the metal, and for the reverse phenomenon on heating, at Ac₁, where, of course instead of a recalescence taking place, an absorption of heat occurs causing the metal to *lose* heat. It is obvious that the term "recalescence" should not be applied to the point Ac₁. The point of recalescence is also called sometimes "recalcscent" point and, seldom, "Gore's phenomenon" (see Historical Sketch at end of chapter). The point Ac₁ has been called point of "decalescence" by some writers and one of them at least refers to it as the "calescence" point.

Critical Range. — Transformation Range. — When the various critical points occurring in steel are considered collectively the range of temperature they cover is frequently called the "critical range," or, more seldom, but very appropriately, the "transformation range." It will soon be shown that the critical range may include one, two, or three critical points. The meaning of the expressions "critical range on heating" and "critical range on cooling" is obvious.

Positions of Ar₁ and Ac₁. — The critical points Ar₁ and Ac₁ do not occur at exactly the same temperature, Ac₁ being generally situated some 20 to 40 deg. higher than Ar₁. When the point Ar₁, for instance, is found at 690 deg. C., the point Ac₁ will generally occur somewhere between 710 and 730 degrees.

¹ The point A of Tschernoff indicated the temperature at which steel suddenly acquires hardening properties on heating or loses them on cooling.

Stead submitted samples of very pure steel containing 0.9 per cent carbon to 16 well-known investigators with the request that they ascertain the Ac_1 and Ar_1 points. The reported results indicated for Ac_1 temperatures varying between 719 and 746 deg., and for Ar_1 temperatures between 697 and 721. This apparently great discrepancy may be accounted for in part at least by the influence of the rate of heating and cooling on the positions of Ac_1 and Ar_1 respectively, as later noted, and by the influence of the temperature from which cooling starts on the position of Ar_1 . Unless standard conditions are maintained in regard to rate of heating and cooling, temperature from which cooling begins and length of time at that temperature, very close agreement between various investigators is not to be expected.

It is also essential that the temperatures recorded should correspond to exactly the same stage of the critical point, namely its beginning or its apex. Howe argues that the beginning of Ar_1 and Ac_1 should be taken as indicating the position of these points on the ground that the beginning of the transformation is less affected by lag. Rosenhain, on the contrary, and his views are shared by the author, contends that the peaks should be read since they represent the temperatures at which the bulk of the specimen undergoes transformation.

In commercially pure carbon steels Ar_1 almost always occurs between 690 and 720 deg. and Ac_1 some 20 to 40 deg. higher. The fact that the critical point on cooling lags behind the point on heating and vice versa, is evidently a case of hysteresis so often observed in physical phenomena and which implies a resistance of certain bodies to undergo a certain transformation, when theoretically the transformation is due, the delayed transformation finally taking place with added violence. This was vividly depicted by Howe some twenty years ago in the case of iron. He wrote: "Just as we can cool water below its freezing-point without completely freezing it, thereby rapidly increasing the strength with which the water tends to freeze, so by a relatively rapid cooling we can carry the metal considerably below Ar_1 , without giving the Ar_1 change time to proceed far, strengthening the while the tendency toward this change, which keeps kindling more and more till it bursts into a blaze, with such evolution of heat as actually to recalesce, to raise the temperature of the metal by some 10 deg., in spite of the continued abstraction of heat by the continued cooling of the furnace."

The slower the heating and cooling the nearer will the two points approach each other, so that with infinitely slow cooling and heating they would undoubtedly occur at exactly the same temperature. If there remained any doubt as to the points Ac_1 and Ar_1 representing the opposite phases of the same phenomenon, i.e. of A being a reversible point, it would suffice to dispel it to consider the fact that in order to induce the retardation Ar_1 the steel must first be heated *past* the point Ac_1 ; and reciprocally the retardation Ac_1 cannot take place unless the metal has first been cooled to a point below Ar_1 . To illustrate: the melting of ice and the freezing of water are undoubtedly the opposite phases of the same phenomenon, each one undoes the work of the other, and in order to freeze the water we must first melt the ice and likewise to melt the ice the water must first be frozen; one change cannot be induced unless the opposite one has last taken place. Indeed it is possible through very slow and undisturbed cooling to lower the temperature of water below its freezing-point before it starts freezing, a clear instance of hysteresis, although in this case called "surfusion," and when freezing takes place the temperature of the water *rises* to its normal freezing-point, a clear case of recalescence although deprived of glow.

The diagram shown in Figure 168 illustrates further this reversibility of the point A_1 . Let two parallel lines represent the phases A_c and A_r of the critical point. Let condition A represent the state of the metal stable above A_c and condition B the state of the metal stable below A_r . The gap between A_c and A_r is due to hysteresis. MN is the temperature at which both the A_c point and the A_r point would occur if there were no hysteresis as, for instance, if the metal could be heated and cooled infinitely slowly. Assuming the metal to be in condition B at a , below A_r , on heating it from a to b above A_c on reaching the A_c point at x it passes from the condition B to the condition A with absorption of heat causing a retardation in the heating; on cooling from b to c , that is to a temperature below A_c but above A_r , the condition A is retained so that upon heating from c to d no transformation can take place at x'

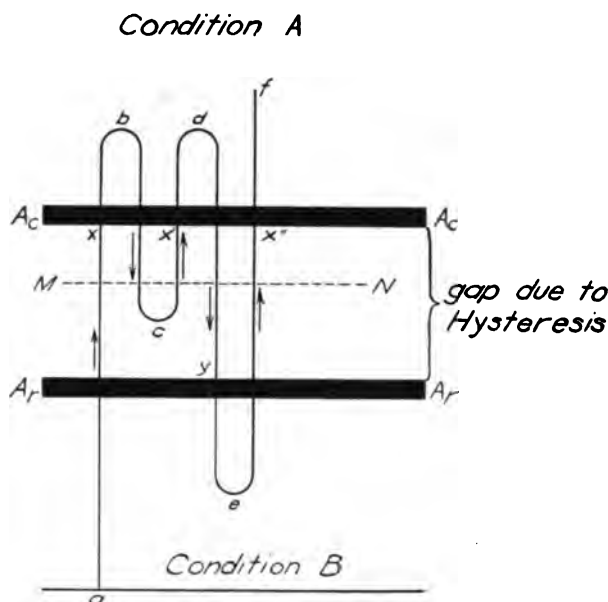


Fig. 168. — Diagram showing reversible critical point.

on passing through the A_c point and therefore no critical point observed. If the metal be cooled from d to e , however, on passing through A_r at y it changes from condition A to condition B with evolution of heat, causing a retardation in the rate of cooling; if it now be heated again from e to f above A_c , a critical point will be observed at x'' since the metal now in condition B will pass to condition A .

It will be evident that between A_r and A_c the metal may be in condition A or condition B depending upon whether it was last cooled from above A_c or heated from below A_r .

Howe uses the notation A_{e1} for the equilibrium temperature for A_1 , that is for the temperature at which the transformation A_r and its reversal, A_{c1} , would both take place, the former on cooling and the latter on heating, in the complete absence of hysteresis. From a very careful weighing of the available data Howe concludes that the position of this equilibrium temperature is probably 723 deg. C.

Speed of Cooling and Heating vs. Position of A_1 . — It has been seen that the

faster the cooling the lower is the position of the point Ar_1 and the faster the heating the higher the point Ac_1 , that is, the faster the cooling and heating the greater the gap between the opposite phases Ar_1 and Ac_1 of the reversible point A_1 .

The cooling of a piece of steel may be so rapid, as in quenching, as to prevent altogether the retardation Ar_1 from taking place, because a low temperature is so quickly reached that the rigidity of the metal prevents the transformation of which Ar_1 is a manifestation. In other words time and a certain amount of plasticity are required for the transformation Ar_1 to occur, and in quenching time is denied when the metal is sufficiently plastic (i.e. at a red heat), while when time is given (i.e. after quenching) the metal has lost its plasticity. It remains untransformed or but partially transformed. It will be shown in another chapter that this suppression of the point Ar_1 is probably the cause of the hardening of carbon steel by sudden cooling.¹

Le Chatelier rightly reminds us that the speed of the transformations occurring at the critical points of steel follows the general laws which govern the speed of all chemical phenomena. In other words that the speed of the transformation is the greater (1) the higher the absolute temperature and (2) the wider the range between the actual temperature and the temperature of equilibrium, that is the temperature at which the transformation is due. Above the critical temperature both influences act in the same direction and the speed of transformation increases without limit. Below the critical temperature these influences act in opposite directions necessarily giving rise to the existence of a maximum speed. According to Le Chatelier this notion of variable speeds of transformation accounts for all the peculiarities of the hardening treatment. On heating it is hardly possible to raise the temperature of transformation more than 100 deg. C. through very rapid heating, while during cooling the speed reaches its maximum at about 600 deg. C., is very feeble below 200, and nearly null at atmospheric temperature.

Temperature from which Cooling begins vs. Position of Ar_1 . — It was first observed by Tschernoff that as the temperature to which steel is heated before being allowed to cool increases, the position of the Ar_1 point is gradually, although slowly, lowered. This influence of what Howe calls the maximum temperature or T^{\max} , has been repeatedly confirmed. Benedicks would explain it on the assumption that at a higher temperature a greater number of nuclei or centers of crystallization are destroyed and that the fewer nuclei left the lower the temperature at which recalescence occurs. Howe believes that the phenomenon may be further explained (1) through the steepening of the thermal gradient during the critical transformation caused by cooling from a higher temperature, (2) through increase of internal pressure resulting from the steepening of the thermal gradient, and (3) through a better diffusion of the pro-eutectoid element and the pearlite element, so that their re-assembling for the purpose of undergoing the transformation in cooling is more difficult.

A long sojourn at a high temperature also appears to have a tendency to lower Ar_1 , while according to Rosenhain the position of Ac_1 is slightly raised if the previous cooling has been very slow and vice versa.

Chemical Composition vs. Position of A_1 . — Generally speaking impurities have a tendency to lower the position of Ac_1 and Ar_1 , some of them decidedly.

According to Howe manganese lowers the Ar_1 point some 24 to 50 deg. C. for each per cent of manganese, while Osmond indicates the position of Ar_1 in a steel con-

¹ It will be explained later that some writers have doubted the suppression of the transformations on rapid cooling and have suggested another explanation of the hardening of steel.

taining 1 per cent of Mn as 685 deg. whereas with 4 per cent of manganese the same point was lowered to 590 deg. It is conceivable that further increase of that element must lower still more the critical point, so that finally it may be lowered below atmospheric temperature, being apparently eliminated. It will be shown in another chapter that this is precisely what occurs in the cases of manganese steel and high nickel steel, containing respectively some 13 per cent of manganese or some 25 per cent of nickel. These steels exhibit no retardation on cooling from a high temperature to atmospheric temperature. When cooled to lower temperatures, however, by immersing them in freezing mixtures or, if need be, in liquid air, the retardations may again occur, at least in the case of nickel steel.

G. H. Clevenger found that 4.5 per cent copper lowers the Ar_1 point of steel containing some 0.5 per cent carbon from 730 to 635 deg. C. or approximately 20 deg. for each per cent of copper. According to J. H. Andrews the absorption of 0.25 per cent of nitrogen by a steel containing 0.6 per cent carbon lowers the point Ar_1 in a marked degree.

In the case of commercial steel of good quality the proportion of impurities, with the possible exception of manganese, varies within relatively very narrow limits, so that no great variation should be expected in the position of the critical point A_1 . Neither is it clear that the amount of carbon present in steel has a marked effect upon the position of the point A_1 , although some writers state that the point is lifted as the carbon increases. As previously stated in pure carbon steel the point Ar_1 almost invariably occurs somewhere between 690 and 720 deg. C. and its reversal Ac_1 20 to 40 deg. higher. Both Ar_1 and Ac_1 would probably occur at about 720 deg. could the cooling and heating be infinitely slow.

Upper Critical Points. — The existence of upper critical points, that is, of thermal retardations occurring at temperatures higher than that of the recalescence point, has already been alluded to. These points were discovered by Osmond and their discovery ushered in a new epoch in the scientific study of iron and steel. To describe these points it is advisable to consider first the thermal retardations occurring in cooling and heating carbonless iron and then similar retardations exhibited by steel containing increasing amounts of carbon.

Thermal Critical Points in Pure Iron. — On cooling from a high temperature, say 1000 deg. C., a piece of the purest iron obtainable and ascertaining its rate of cooling as previously explained, the metal is found to cool normally, i.e. at a uniformly retarded rate, until a temperature of some 900 to 880 deg. C. is reached when a marked retardation is observed in the rate of cooling, indicating a spontaneous evolution of heat, in this case, however, insufficient to cause an actual rise of temperature, i.e. a recalescence of the metal. The cooling then resumes, or nearly resumes, a normal rate of cooling, until at about 760 deg. C. a second evolution of heat takes place causing another retardation in the rate of cooling, not so marked, however, nor so sharply defined as the first one. The metal then cools normally or quite so to atmospheric temperature. We have thus detected two unmistakable spontaneous evolutions of heat in the cooling of pure iron. The corresponding critical points are called Ar_3 and Ar_2 , the latter symbol indicating the lower point. It should be noted that the recalescence point which should occur at some 700 deg. is here absent. Carbonless iron has no point of recalescence.

These two upper points like the point of recalescence are reversible critical points, i.e. on heating the opposite phases of the transformations (whatever those trans-

formations may be) take place with absorption of heat, causing a retardation in the rate of heating and the corresponding points being designated by the symbols Ac_3 and Ac_2 . The point Ac_3 occurs at a temperature some 10 to 30 deg. higher than its reversal Ar_3 , while Ac_2 occurs at nearly the same temperature as Ar_2 .

Dr. J. K. Burgess and J. J. Crowe (Bulletin American Inst. Mining Engineers, October, 1913, p. 2537) made a large number of determinations of the critical points of the purest irons obtainable using great refinement in manipulations, and found Ac_3 to occur at 909 deg. C., Ar_3 at 898 deg. and Ac_2 and Ar_2 both at 768 deg.

Peculiarities of the Point A_2 . — The point A_2 is generally less marked than the points A_3 and A_1 . Unlike A_3 its position is little affected by the carbon content, and unlike A_3 and A_1 the point on heating, Ac_2 , occurs at nearly the same temperature as the point on cooling, Ar_2 . To these peculiarities must be added another one, namely, the fact that A_2 appears to cover a wide range of temperature. While its intensity decreases with fall of temperature its lower limit probably extends to considerably below 700 deg. In other words the transformation of which A_2 is a manifestation is not completed by the time the point A_1 is reached. Indeed Osmond mentions 550 deg. C. as the probable lower limit of the point A_2 . Some explanations of these peculiarities of the point A_2 will soon be offered.

Arnold insists that with satisfactory apparatus the point Ar_2 always shows a double peak, the upper one at about 765 deg., the lower at 752 deg. This statement is generally opposed by the results of other investigators. None of the 130 curves, for instance, taken with the greatest care and skill by Dr. Burgess shows a double peak at Ar_2 .

Thermal Critical Points in Very Low Carbon Steel. — Let us now take a sample of steel containing some 0.10 per cent carbon, and let us ascertain its rate of cooling from a high temperature precisely as before. Three thermal retardations will be detected, Ar_3 at about 850 deg., Ar_2 near 760 deg., and Ar_1 (point of recalescence) near 700 deg. Of these three spontaneous evolutions of heat the upper one at Ar_3 will be the most marked, while at Ar_2 and at Ar_1 they will be quite faint, their satisfactory detection calling for the use of delicate instruments and careful manipulations. On heating corresponding retardations will occur, due to spontaneous absorptions of heat, the resulting critical points being designated as Ac_3 , Ac_2 , and Ac_1 . Of these Ac_3 and Ac_1 will occur at temperatures some 20 deg. or more higher than Ar_3 and Ar_1 , while Ac_2 will occupy nearly the same position as Ar_2 on the temperature scale, that is about 760 deg.

Thermal Critical Points of Medium High Carbon Steel. — The determination of the rate of cooling of a steel containing some 0.45 per cent carbon reveals the existence of two critical points, one, evidently the point of recalescence, Ar_1 , at the usual temperature (680 to 720 deg.) and one upper point in the vicinity of 740 deg. Does the presence in this steel of only one upper point mean that one of the two upper points detected in carbonless iron and in very low carbon steel has disappeared, because of the presence of more carbon, or does it mean that the two upper points have now united into a single one? The latter view is generally assumed to be the correct one and this single upper point of medium high carbon steel is designated accordingly by $Ar_{3.2}$. This notation clearly implies that the two distinct evolutions of heat which in carbonless iron and in very soft steel occur separately at Ar_3 and Ar_2 here occur at one and the same temperature. Increasing the carbon content

decreases the interval of temperature between the two upper points until, finally, for a certain carbon content the points meet to form the double point $A_{3.2}$.

Merging of A_3 and A_2 . — It has been seen that as the carbon increases the point A_3 is gradually lowered until finally it merges with A_2 , whose position is not greatly affected by the presence of carbon, to form the point $A_{3.2}$. It would be interesting to know the exact proportion of carbon required to cause this merging. This, however, is difficult to ascertain because of the experimental difficulty of separating two critical points situated very near each other as they must be in the vicinity of the merging point, and also because this merging will be shifted somewhat by speed of heating and cooling and by slight changes of chemical composition. According to A. Meuthen's calorimetric work later referred to, A_3 and A_2 merge for a carbon content corresponding to 0.32 per cent, while Howe indicates 0.438 per cent carbon as the probable merging point. From the mass of experimental evidences which have been published it seems probable that in commercial steels the merging takes place at about 0.30 per cent carbon.

Equilibrium Temperatures for A_3 and $A_{3.2}$. — Howe uses the notations Ae_3 for the equilibrium temperature for A_3 , that is the temperature at which the transformation Ar_3 on cooling and its reversal, Ac_3 on heating, would take place in the complete absence of hysteresis. A close examination of the available data leads to the conclusions that the position of Ae_3 is given by the formula

$$T^\circ = 917 - 306 \times C$$

in which C represents the percentage of carbon in the steel and T the temperature in degrees C. for Ae_3 .

For the equilibrium temperature of $A_{3.2}$ Howe gives the formula

$$T^\circ = 820 - 105.5 \times C$$

Thermal Critical Point in Eutectoid Steel. — Eutectoid steel, that is steel containing some 0.85 per cent of carbon, exhibits but one critical point, the point of recalescence, very marked at about 700 deg. C. on cooling. Shall it be inferred from the occurrence of this single point that in eutectoid steel the transformations of which the upper points A_3 and A_2 or the double point $A_{3.2}$ are manifestations do not take place? Or shall it be assumed that these transformations now take place at the same temperature as the transformation corresponding to the critical point A_1 ? In other words that increasing the amount of carbon has so depressed the position of the two upper points as to cause them to unite with the lower point, forming now a triple point to be designated as $Ar_{3.2.1}$? This is the view generally held. The critical point on heating is designated by the notation $Ac_{3.2.1}$. It will be explained in another chapter why the points A_3 , A_2 , or $A_{3.2}$ cannot exist in eutectoid or hyper-eutectoid steel, when it will also be shown that the single point of eutectoid steel is not in fact a merging of A_3 , A_2 , and A_1 , but merely the point A_1 , the upper points having disappeared.

Merging of $A_{3.2}$ and A_1 . — As the carbon content of the steel increases still more after the merging of A_3 and A_2 has been effected, the interval between the points $A_{3.2}$ and A_1 gradually diminishes until these two points, in turn, appear to merge to form the triple point $A_{3.2.1}$. Theoretically this apparent merging should occur when the steel is composed entirely of pearlite, that is, when it contains in the vicinity of 0.85 per cent carbon, for reasons that will later be made clear. As a matter of fact,

however, the merging seems to take place long before so large a proportion of carbon is present, for the point $A_{3.2}$ is seldom detected in steel containing more than some 0.50 or 0.60 per cent of carbon; this is probably due, as already explained, to the difficulty of separating, experimentally, two critical points so close to each other.

Factors Influencing the Positions of the Upper Points A_3 and A_2 . — It has been made clear that as the carbon increases the point A_3 is gradually lowered until with some 0.30 or 0.40 per cent carbon it merges with the A_2 point, while the resulting double point $A_{3.2}$ is further lowered with increasing carbon and merges with the A_1 point at about 0.85 per cent carbon. The position of the A_2 point on the contrary so long as that point remains independent, that is, in alloys containing less than some 0.40 per cent carbon, is unaffected by variations in carbon content. Like the points of recalescence, the upper points on cooling Ar_3 , Ar_2 , and $Ar_{3.2}$ are probably lowered (1) by rapid cooling, (2) by increasing the temperature from which cooling starts, (3) by a long sojourn at a high temperature, and (4) by the presence of notable proportions of some elements such as manganese, nickel, silicon, etc., while the corresponding points on heating Ac_3 , Ac_2 , and $Ac_{3.2}$ are probably slightly raised by increased speed of heating.

P. Oberhoffer reports that one per cent of manganese lowers the point A_3 or $A_{3.2}$ about 70 deg. C. while Charpy and A. Cornu (Comptes Rendus, 1913, Vol. CLVII, p. 319) found (1) that the point A_3 of iron and low carbon steel vanishes when the silicon-content reaches 1.5 per cent and (2) that the point A_2 remains distinct but that each increase of one per cent of silicon lowers its position by about 11 deg. C.

Thermal Critical Points in Hyper-Eutectoid Steel. — Carefully conducted observations reveal the existence of an upper critical point in hyper-eutectoid steel, at least in steel containing a decided amount of free cementite and, of course, of the point of recalescence. It seems proper to designate this upper point by the symbol A_{cm} (Ar_{cm} on cooling, Ac_{cm} on heating) for reasons later to be given, cm standing for cementite. At least one writer, however, has designated this point on cooling by the notation Ar_{mc} , mc standing for massive cementite. Other writers have called it an A_3 point, a notation from which one would naturally infer that this upper point of hyper-eutectoid steel is similar to the upper point of iron and of very low carbon steel, which is not the case.

Purely theoretical considerations lead us to infer that the position of the point A_{cm} is lowered as the proportion of carbon decreases, finally merging with the point $A_{3.2.1}$ at the eutectoid point. It would follow from this that the single point of eutectoid steel is really a merging of four points A_3 , A_2 , A_1 , and A_{cm} and that it should accordingly be designated by $A_{3.2.1 cm}$. It is, however, the universal custom to ignore this contribution of A_{cm} to the single point of eutectoid steel and to use for the latter the notation $A_{3.2.1}$.

The amount of heat evolved at Ar_{cm} is very slight, hence the difficulty of detecting this point. Carpenter and Keeling ascertained its existence in steels containing respectively 1.31, 1.51, 1.69, 1.85, and 1.97 per cent carbon at the following corresponding temperatures: 883, 911, 985, 1030, and 1042 deg. C. With lower carbon contents, that is, nearer the eutectoid composition, the heat evolved is so slight that the detection of Ar_{cm} as a separate point is quite impossible. In theoretical diagrams, however, the existence of this point is always indicated in all hyper-eutectoid steels with a sharp merging with $A_{3.2.1}$ at the eutectoid point.

The point Ar_{cm} then should occur in all hyper-eutectoid steels at temperatures

increasing from some 700 to 1050 deg. C. as the carbon increases from 0.85 to 2.00 per cent.

Merging of $A_{3.2.1}$ and A_{cm} . — As already explained theoretically the merging of the points $A_{3.2.1}$ and A_{cm} should take place at the eutectoid composition, that is, for steel containing in the vicinity of 0.85 per cent carbon. Experimentally, however, the point A_{cm} cannot be detected in steel containing less than some 1.20 per cent carbon. Bearing in mind that hypo-eutectoid steels containing more than 0.60 per cent carbon or thereabout have likewise but one critical point so far as experimental evidences are concerned, it will be seen that for all practical purposes we may consider all grades of steel containing from 0.60 to 1.20 per cent carbon as having but one critical point, namely, the point of recalescence, at some 700 deg. C. on cooling, although theoretically eutectoid steel only should have but one such point.

Minor Critical Points. — Some experimenters believe to have discovered some critical points other than those so far described. These points, which may be referred to as minor critical points, correspond to very faint evolutions or absorptions of heat, and produce, therefore, but very slight jogs in the thermal curves. Their existence is not fully established and they appear to have but little if any influence upon the practical side of our subject. They should, however, be mentioned in these pages so that the student may at least have some idea of their nature and claims to recognition. Roberts-Austen in 1898 detected a slight evolution of heat between 550 and 600 on cooling in iron and hypo-eutectoid steel, and this point was again detected by Carpenter and Keeling in 1904. The latter observers named it the Ar_0 point, following in this Roberts-Austen.

Roberts-Austen detected another evolution of heat in pure iron between 450 and 500 deg. C. the existence of which he ascribed to the presence of hydrogen resulting in a separation of hydroxide of iron taking place at this critical point. Finally the same observer described one more slight evolution of heat in pure iron at about 270 deg. C. which he tentatively ascribed to the formation of an iron-iron hydroxide eutectic.

Arnold believes in the existence of a critical point between A_3 and A_2 , of maximum intensity when the steel contains some 50 per cent of pearlite (about 0.45 per cent carbon) which he thinks is due to the formation or segregation of pearlite and hardenite, a constituent later to be described.

Data Showing the Position of the Critical Points. — A very comprehensive set of determinations of the critical points of iron and steel was made by Carpenter and Keeling. Their results are tabulated on page 168. The table includes the critical points occurring during the solidification period of the various steels and irons investigated. These will be considered in another chapter. The position of the critical points as determined by Burgess, Stead, and others has already been indicated. There is substantial agreement between the results of these investigators.

Relative Quantities of Heat Evolved or Absorbed at the Critical Points. — The various critical points that have been considered in the preceding pages do not indicate evolutions or absorptions of equal quantities of heat; they are not of equal intensity. The point A_3 is very marked and sharply defined in carbonless iron but decreases rapidly in intensity as the carbon increases. The point A_2 is relatively feeble and not very sharply defined and as already mentioned shows a tendency to cover a considerable range of temperature. Its intensity, moreover, is little affected by the carbon content of the steel. The point $A_{3.2}$, being a merging of A_3 and A_2 , is more intense than A_2 but less intense than A_3 in carbonless iron owing to the fact that when the merging takes place the A_3 point has lost much of its intensity. The point A_1 is feeble in very low carbon steel, but its intensity increases rapidly with the carbon content, becoming so great as to cause the metal to glow or recalesce as previously described and being maximum for steel of eutectoid composition. These

differences in the thermal values of the critical points will be explained in another chapter.

A. Meuthen (Ferrum, 1912, Vol. X, p. 1) found by careful calorimetric experiments (1) that one gram of pearlite requires 15.9 calories for its transformation into austenite (a transformation which occurs at Ac_1 or $Ac_{3.2.1}$, as explained in the following chapter); (2) that the transformation of one gram of β iron into α iron develops 5.6 calories (a transformation which occurs at Ar_2); (3) that the transformation (at Ar_3) of one gram of γ iron into β iron also develops 5.6 calories; and (4) that the separation of one gram of α iron (free ferrite) from the solid solution (austenite), a separation which occurs *between* Ar_3 and Ar_1 , produces 14.1 calories.

Graphical Representation of the Position and Magnitude of the Critical Points. —

The position of the critical points corresponding to various percentages of carbon is illustrated graphically in Figure 169. The diagram refers to the critical points on cooling, i.e. the Ar points, and it should be borne in mind that the corresponding points on heating, the Ac points, occur some 20 to 40 deg. higher, with the exception of the point Ac_2 which seems to occupy nearly the same position as the point Ar_2 . An attempt has been made in this diagram to indicate the relative intensities of the various points by shaded areas of proportional thickness on both sides of the lines indicating their position. This is based chiefly on theoretical considerations and is in accordance with the generally accepted views regarding the causes of the critical points as explained in the next chapter. An examination of the diagram shows (1) that the point Ar_3 intense in carbonless iron decreases gradually in intensity as the carbon increases, (2) that the intensity of Ar_2 is not greatly affected by the carbon content, (3) that $Ar_{3.2}$ fairly intense at first becomes rapidly feebler and finally disappears just as it meets Ar_1 , (4) that Ar_1 at first very faint becomes more marked with increased carbon, being maximum for a carbon content of some 0.85 per cent (the eutectoid point), (5) that the point $Ar_{3.2.1}$ very intense at the eutectoid point gradually loses some of its intensity, although always remaining pronounced, and (6) that the point Ar_{cm} very faint near the eutectoid composition increases in intensity with the carbon content.

These theoretical inferences are well supported by experimental evidences in the case of the magnitude of the points Ar_1 and $Ar_{3.2.1}$ and quite satisfactorily in regard to Ar_3 and Ar_{cm} . They ascribe to the points Ar_2 and $Ar_{3.2}$, however, a magnitude and a sharpness which is not borne out by experiments as later explained when it will also be seen that some writers doubt the accuracy of the explanation generally offered to account for the point A_2 .

The diagram, therefore, while undoubtedly useful, is probably but approximately accurate and likely to be modified with increased knowledge of the facts it aims to depict.

Determination of the Thermal Critical Points. — The thermal critical points are universally determined by means of the Le Chatelier thermo-electric pyrometer. Indeed it is the invention of this invaluable instrument that made the detection of the upper critical points possible. Had it not been invented we probably would still be in ignorance of the existence of the upper points, while we would have but little knowledge of the exact position of the point of recalescence.

Cooling and Heating Curves. — The determination of the thermal critical points calls for the construction of heating and cooling curves. In these curves successive falls (or rises) of temperature, say of 10 deg. C., $\theta - 10$, $\theta - 20$, $\theta - 30 \dots$ are plotted

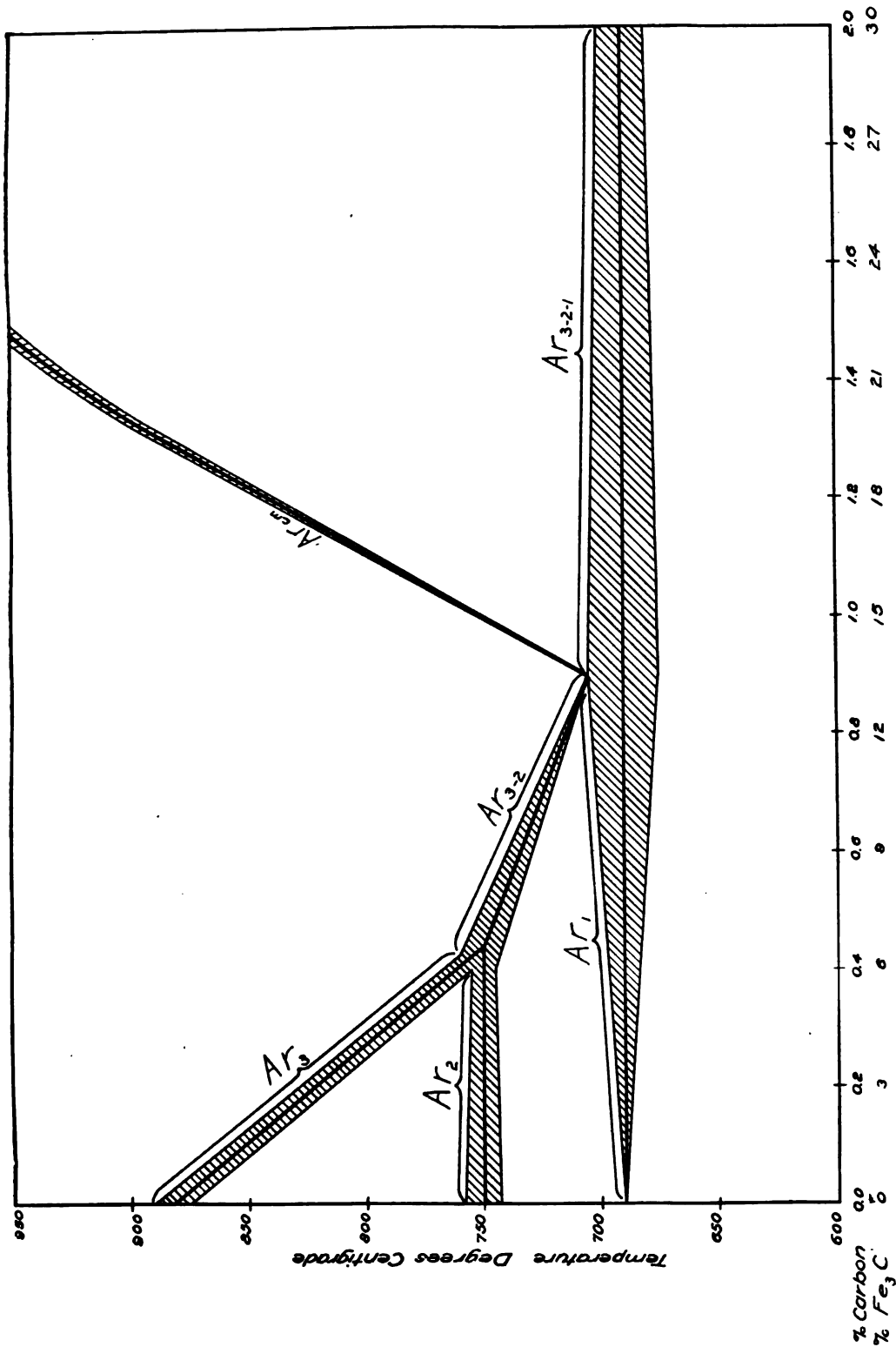


Fig. 169. — Diagram showing the position and magnitude of the critical points.

as ordinates, while as abscissæ are plotted (a) the corresponding time intervals in seconds, $t, t', t'', t''' \dots$ elapsed since the beginning of the observation, or (b) the actual intervals of time $t' - t, t'' - t', t''' - t'' \dots$ required for each noted fall of temperature. In other words the coordinates are θ and t in the first instance, θ and dt in the second. The curve obtained by the first method is known as a time-temperature curve while the second method yields an inverse rate curve.¹

Time-temperature curves representing the heating and cooling of pure iron are shown in Figure 170. While in these curves the evolutions or absorptions of heat cor-

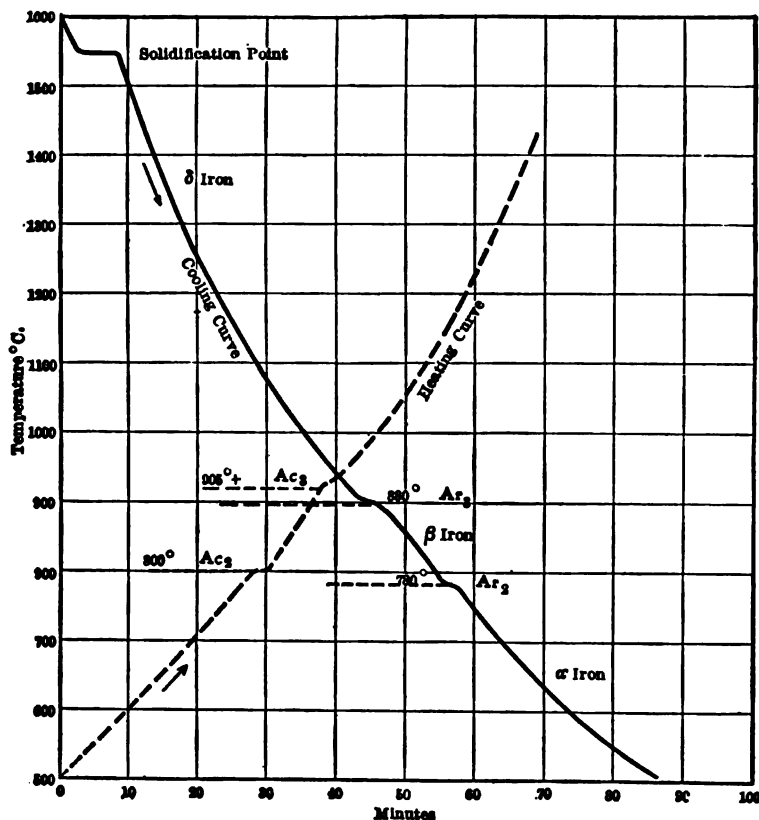


Fig. 170. — Time-temperature curves. Heating and cooling of pure iron. (Görens.)

responding to the points A_3 and A_2 can be detected, they do not stand out very conspicuously, and it may well be feared that slight thermal retardations might escape detection in curves of this kind since they would cause but very slight jogs in the curve. These considerations led Osmond to adopt the inverse rate method for the plotting of thermal curves. Curves of this type are shown in Figures 171 and 172.

¹ It is evident that similar curves would result from reversing the observations, i.e. noting the successive falls of temperatures $\theta, \theta', \theta'' \dots$ corresponding to equal intervals of time, say of 15 seconds, $t + 15, t + 30, t + 45 \dots$ and plotting the former as ordinates and the latter as abscissæ. The coordinates in this case would be $d\theta$ and t .

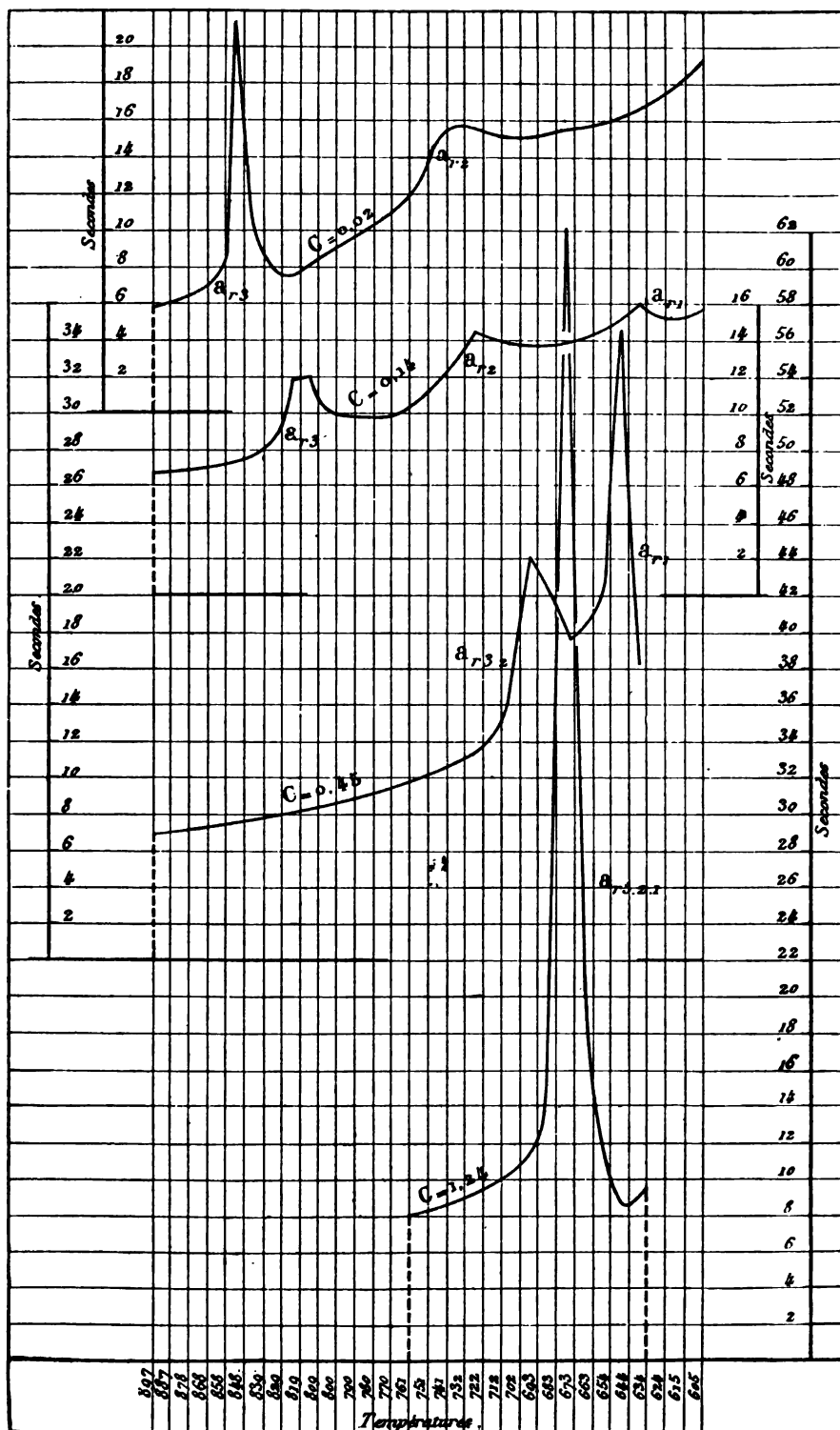


Fig. 171. — Inverse rate curves. Cooling of steels containing respectively 0.02, 0.14, 0.45, and 1.24 per cent carbon. (Osmond.)

The thermal points correspond to sharp peaks in the curves, the lengths of which are roughly proportional to the amount of heat evolved on cooling or absorbed on heating. This method is quite universally applied unless, as later explained, a neutral body is used for the determination of the critical points.

Use of Neutral Bodies.—The method described above for the detection of the thermal critical points is open to the objection that the rate of cooling or heating of the steel under observation is necessarily affected by any irregularity in the cooling or heating of the furnace itself and by other outside agencies. These disturbing factors introduce irregularities in the thermal curves which may render their interpretation difficult and may indeed altogether hide the existence of critical points where but a very small amount of heat is evolved or absorbed. Again, on cooling for instance, when a critical point is reached the temperature of the metal is affected in opposite directions (1) by the cooling furnace which has a tendency to lower its tem-

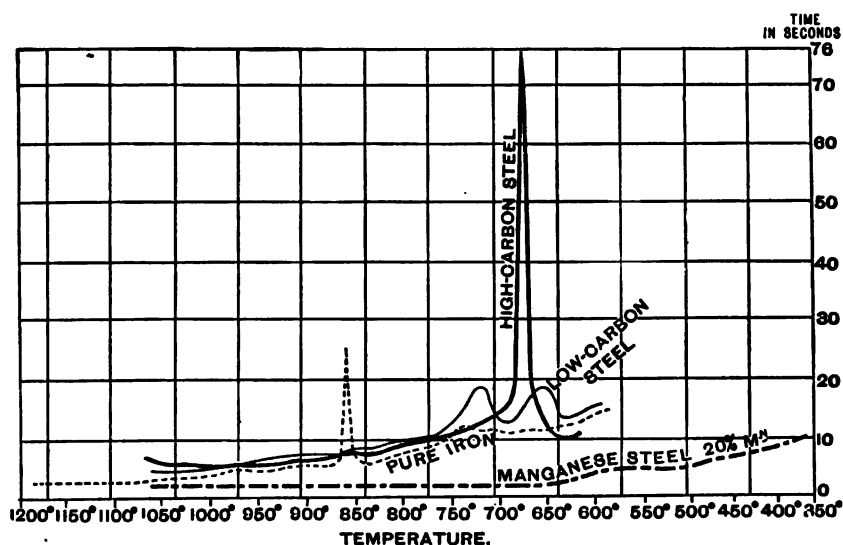


Fig. 172. — Inverse rate curves. Cooling of pure iron, low carbon steel, high carbon steel, and manganese steel. (Roberts-Austen.)

perature and (2) by the evolution of heat occurring at the critical point, the effect of which is to raise its temperature. It is evident that the cooling influence of the furnace has a tendency to decrease the apparent magnitude of the critical point and therefore to mask it.

The elimination of these objectionable influences should result in sharper thermal curves and in the detection of faint evolutions or absorptions of heat. This was accomplished by Roberts-Austen through the use of a neutral body and double thermocouple so connected that the difference of temperature between the metal under investigation and the neutral body is recorded, as well as the actual temperature of the metal.¹ If the heat capacities and emissivities of the metal and of the neutral piece were identical their temperature would be exactly the same except at the crit-

¹ For the arrangement of the galvanometers, connections, etc., see the description of the Saladin-Le Chatelier-Pellin instrument, Chapter I.

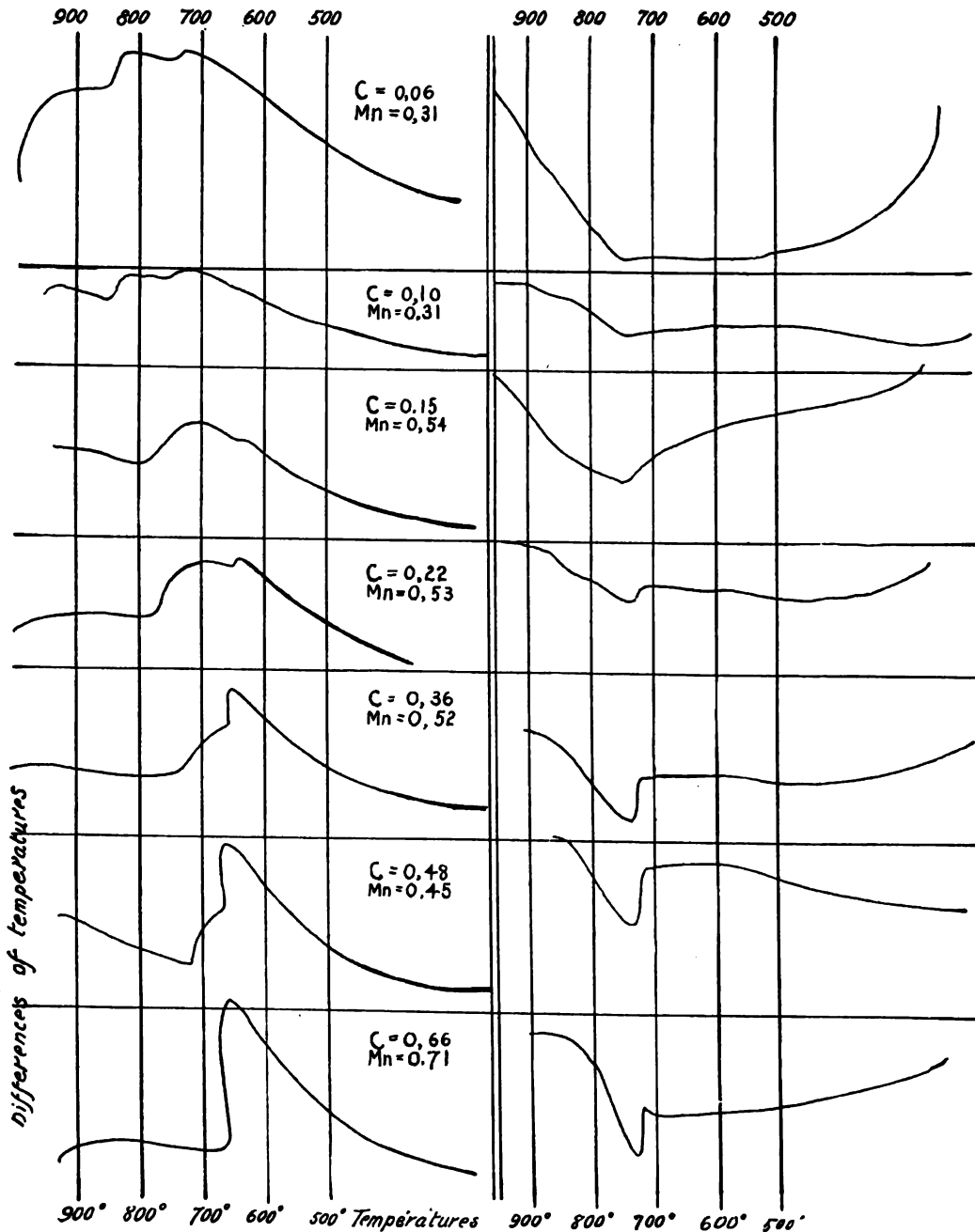


Fig. 173. — Difference curves. Cooling and heating of various steels. (Saladin.)

ical points, when heat is evolved or absorbed by the metal while the neutral body is, of course, free from any such thermal disturbance. Any difference of temperature between the two pieces, therefore, would indicate a critical point. Since it is generally impossible, however, to use a neutral body having exactly the same heat capacity as that of the metal under observation, it will be apparent that there will always be a

difference between the temperatures of the two pieces, one always lagging behind the other, and that the critical points will correspond to sudden increase in the difference between their respective temperatures. Since, however, the critical points are now caused solely by abrupt differences between the temperatures of the two bodies, they are freed from the irregularities mentioned above as well as from the masking influence of the falling or rising temperature of the furnace, seeing that both pieces are now equally affected, and the curves obtained should indicate more sharply and conspicuously the existence of even faint absorptions or evolutions of heat.

The neutral body should, of course, be free from any thermal transformation within the range of temperature covered by the experiments. Platinum, porcelain, clay, 25 per cent nickel steel, and (by the author) austenitic manganese steel have been used. The plotting of the thermal curves when a neutral body is used may be

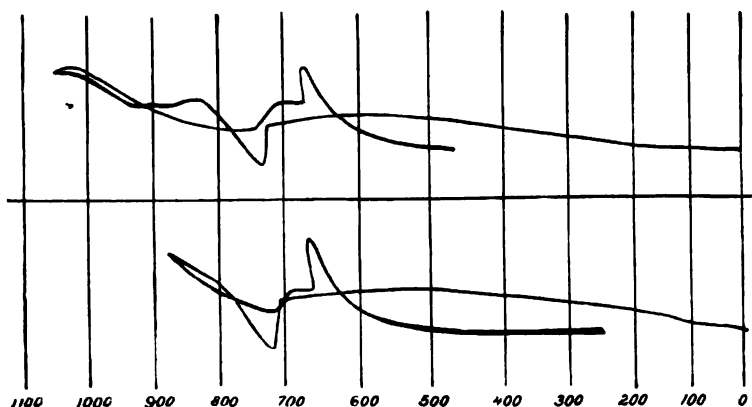


Fig. 174. — Difference curves. Cooling and heating curves taken on same photographic plate. (Saladin.)

done in two different ways, (1) successive falls (or rises) $\theta - 10, \theta - 20, \theta - 30 \dots$ of the temperature of the metal as indicated by one of the galvanometers may be plotted as ordinates against the corresponding differences in temperature $\theta - \theta_1, \theta' - \theta'_1, \theta'' - \theta''_1 \dots$ of the two cooling bodies, as indicated by the second galvanometer, the coordinates in this case being θ and $\theta - \theta_1$, and the curve known as a "difference" curve, or (2) according to Rosenhain, successive falls of temperature may be plotted as ordinates against the corresponding rate of cooling for each degree of temperature $\frac{\theta - \theta_1}{\theta}, \frac{\theta' - \theta'_1}{\theta'}, \frac{\theta'' - \theta''_1}{\theta''}$ as abscissæ, the coordinates being in this method θ and $\frac{d(\theta - \theta_1)}{d\theta}$ and the curve known as a "derived differential" curve.

Difference curves are shown in Figures 173 to 175. The curves of Figures 173 and 174 were taken with a Saladin-Le Chatelier-Pellin instrument. Figure 173 shows the critical points on heating and cooling of a series of carbon steels containing from 0.06 to 0.66 per cent carbon, the cooling and heating curves having been taken on separate photographic plates. In Figure 174 are shown the heating and cooling curves taken on the same plate of two steels containing respectively 0.36 and 0.46 per cent carbon.

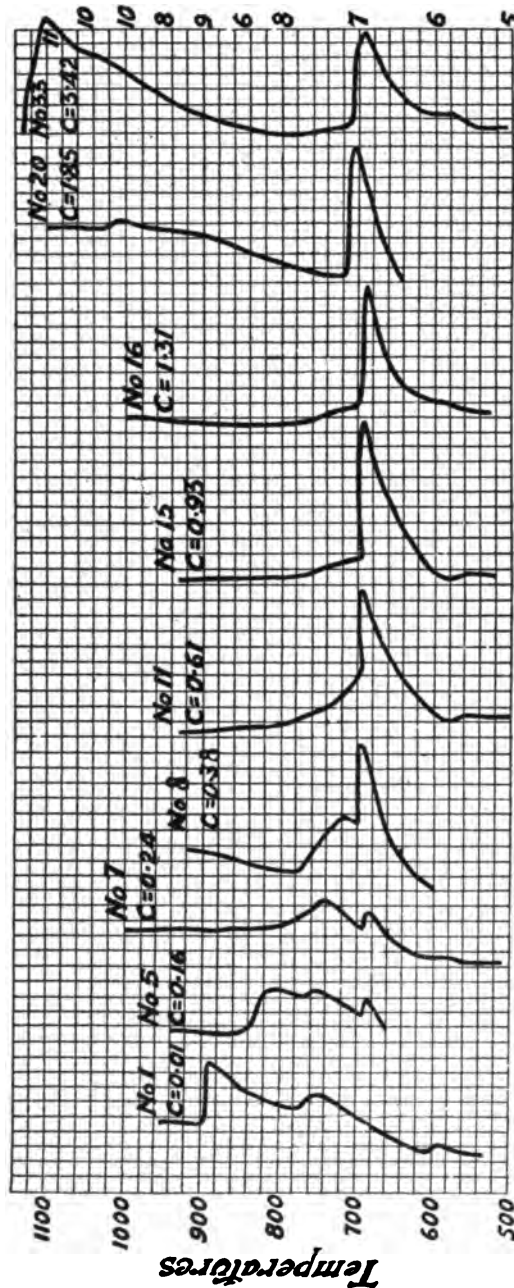


Fig. 175. — Difference curves. Cooling of a series of very pure carbon steels. (Carpenter and Keeling.)

The curves of Figure 175 are difference curves of a series of very pure carbon steels taken by Carpenter and Keeling.

The purpose of Rosenhain's derived differential method of plotting is to eliminate the irregularities from which difference curves still suffer and which are due chiefly to differences between the heat capacities and emissivities of the sample and neutral

body resulting in differences in their rates of cooling and heating. The resulting curves cannot, of course, be autographically recorded. They call for the replotted of the data afforded by the difference (θ vs. $\theta - \theta_1$) curves. Some of Carpenter and Keeling's results replotted by Rosenhain according to his derived differential method are shown in Figure 176.

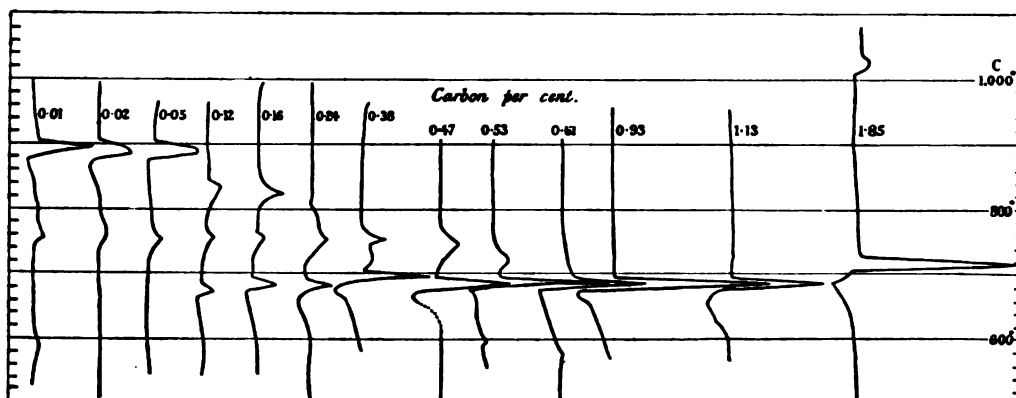


Fig. 176. — Derived differential curves of carbon steels replotted from the data of Carpenter and Keeling. (Rosenhain.)

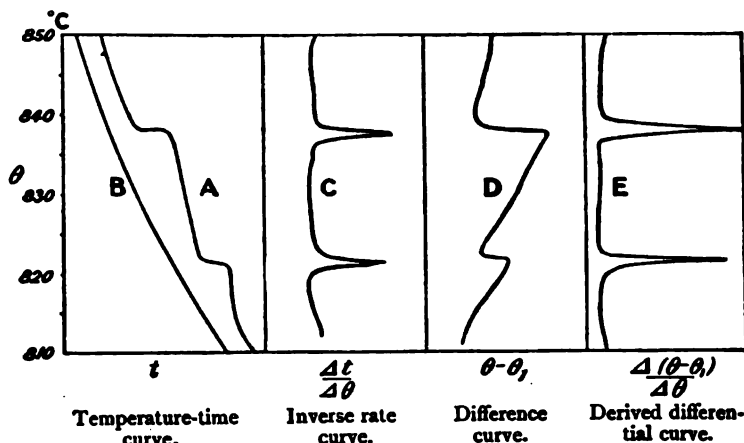


Fig. 177. — Different types of cooling curves. (Desch.)

Additional Illustrations of Cooling Curves.—The different types of cooling curves described in the preceding pages are well illustrated in Figure 177. These curves were constructed from the data given in the following table, in which each unit in t represents intervals of time of 15 seconds, θ the corresponding temperatures of the sample, and $\theta - \theta_1$ corresponding differences of temperature between the sample and a neutral body cooling under identical conditions. The curve B , representing the cooling curve of a neutral body free from critical transformations, has been added for comparison.

t	θ	$\theta - \theta_1$	t	θ	$\theta - \theta_1$
5	850.0°	8.5°	18	829.0°	11.0°
6	848.0	8.5	19	825.0	8.2
7	844.7	7.5	19.5	823.3	7.3
8	842.0	7.0	20	822.2	6.7
9	839.5	6.3	21	821.7	7.7
10	838.5	7.0	22	821.5	8.5
11	838.2	8.8	23	821.3	9.8
12	838.1	10.2	24	821.1	10.1
13	838.0	12.0	24.5	819.0	9.5
14	837.9	13.6	25	815.0	6.0
15	837.5	15.5	26	813.0	5.0
16	836.0	14.6	27	811.6	4.7
17	833.0	13.0			

Self-Recording Pyrometers. — With the use of neutral bodies self-recording instruments are generally employed. The Saladin-Le Chatelier-Pellin autographic pyrometer has been described in Chapter I. The self-recording may be by means of photographic plates or by some other mechanical devices. The former method calls for the use of mirror galvanometers sending a beam of light upon the photographic plate while in other autographic recorders, needle galvanometers are used. The relative merits between photographic recorders and other types are summed up by Burgess as follows:

“It is evidently of great advantage to use self-recording apparatus when possible, and it then becomes necessary to choose between the photographic type and the autographic. The latter possesses the advantage that the experimenter may watch any part of the record, and can therefore control the operation and at any moment vary the conditions affecting the experiment; whereas with a photographic recording apparatus, as usually constructed, the observer does not know whether or not the experiment is progressing properly until it is finished and he has developed the sensitive plate. The manipulation by the photographic method is usually also more delicate and time consuming and the adjustment less sure, and the record often requires further graphical interpretation. The autographic method is in general not adapted for interpreting phenomena taking place within an interval of a few seconds, so that for very rapid cooling it is necessary to employ the photographic method. It is possible to construct the photographic recorder so as to obtain a very considerable range of speeds with the same apparatus, while it is difficult and costly to construct an autographic recorder having more than two speeds.”

Other Methods for the Determination of the Critical Points. — The spontaneous evolutions or absorptions of heat observed at the critical points are obviously manifestations of transformations taking place within the metal and it will be seen in the next chapter that many other properties of iron and steel undergo at these temperatures sudden and marked changes. It is obvious, therefore, that the determination of the change taking place in any one of these properties in function of the temperature will afford a means of detecting the existence and location of the critical points. The method fully described in the preceding pages, and by far the most generally used, may be termed the “thermal method.” Other methods based on the discon-

tinuity in the variation of certain properties occurring at the critical points will now be briefly described.

Metallographic Method for the Determination of the Critical Points. — Howe and A. G. Levy have used, with marked success, a metallographic method for the determination of the critical points, notably of the point A_3 . The method for Ac_3 consists in noting the temperature at which the re-absorption of ferrite is found to be complete, and for Ar_3 , the temperature at which rejection of ferrite begins. It will be explained in the next chapter that these phenomena correspond to the occurrence of the Ar_3 and Ac_3 points. The samples of hypo-eutectoid steels are first heated to a high temperature (1200 to 1450 deg.) and slowly cooled in the furnace in order to assemble the ferrite into coarse masses. Specimens of this coarsened steel are then heated to various temperatures below and above the supposed position of Ac_3 holding the temperature stationary for from 30 to 60 minutes. The specimens are then quenched and preferably reheated to some 300 or 400 deg. in order to convert the martensite into troostite and thus secure greater contrast between the free ferrite and the matrix into which it is embedded and hence readier distinction of small amounts of free ferrite. These structural changes are explained in Chapters XVI and XVII. The Ar_3 point is determined in a similar manner by noting the temperature at which free ferrite first makes its appearance in cooling down. The successive heatings may be 10 deg. apart.

Calorimetric Method for the Determination of the Critical Points. — A. Meuthen (Ferrum, 1912, Vol. X, p. 1) has determined by the vacuum method of Oberhoffer (Bunsen ice calorimeter and electric resistance furnace) the quantities of heat evolved when iron carbon-alloys cool through their critical points and the method may be used for the determination of these points.

Thermo-Electric Method for the Determination of the Critical Points. — W. Broniewski (Comptes Rendus, 1913, Vol. CLVI, p. 1983) has applied a thermo-electric method to the determination of the critical points which he considers at least equal in accuracy to other methods. It consists in determining the thermo-electromotive force of the iron or steel in relation to copper. The occurrence of discontinuity in the variations of the electro-motive force indicates the positions of the critical points. With 0.07 per cent carbon the point A_2 was found at about 730 deg. In pure iron A_3 occurred at 950 deg. and in steel with 0.07 per cent carbon its position was 850 deg. With more than 0.44 per cent carbon the points A_2 and A_3 were merged with the recalescence point.

Melting-Points Method for the Determination of the Critical Points. — Stead has devised an ingenious method for the determination of the critical points Ar_1 and Ac_1 (Journal Iron and Steel Institute 1913, II, p. 399) by which the use of pyrometers may be dispensed with, the method being based on the known melting-point of sodium chloride and of some metals in the form of wire.

Magnetic Method for the Determination of the Critical Points. — It will be explained in the following chapter that iron-carbon alloys lose their ferro-magnetism, or at least the bulk of it, on heating in passing through the points Ac_2 , $Ac_{3.2}$, or $Ac_{3.2.1}$ as the case may be, and recover it in cooling at the points Ar_2 , $Ar_{3.2}$, or $Ar_{3.2.1}$. By observing these magnetic transformations and noting the temperatures at which they occur, the position of the critical points may be accurately determined. The author has found the following procedure very satisfactory. A (Fig. 178) is an electric resistance furnace; DD two round bars of iron (the author uses American ingot iron, a

product nearly free from carbon) suitably held in position; C is the piece of iron or steel the magnetic critical points of which are to be determined; X is the hot junction of a thermo-electric couple introduced into a hole drilled in the sample C; E is an electro magnet surrounding a portion of the bar D; G is an iron needle so balanced that it is readily attracted by the end H of the composite bar DCD when the latter is magnetized. As long as the temperature of the piece C remains below its Ac_2 point (or $Ac_{3.2}$, or $Ac_{3.2.1}$ according to the carbon content) the bar DCD attracts the needle

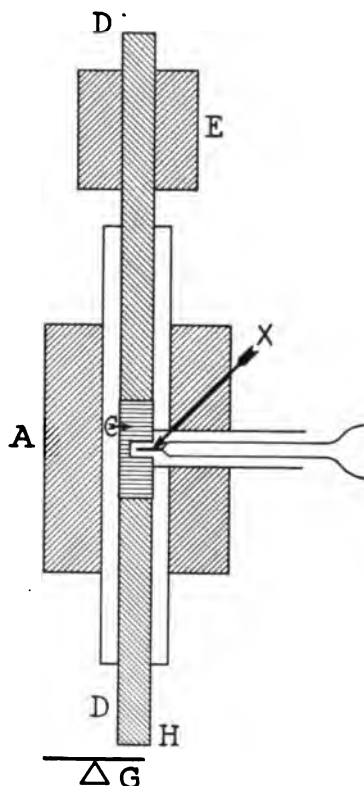


Fig. 178. — Magnetic test for the determination of the thermal critical points in iron and steel.

or keeper G but when the critical point is reached the magnetic flux ceases to pass through C and the needle drops. The point on heating is in this way sharply recorded. On cooling as soon as the point Ar_2 is reached the steel recovers its magnetism and the needle G is again attracted. The method is sufficiently delicate to detect the A_2 point in carbonless iron, and in very low carbon steel.

Historical. — A brief historical sketch of the discovery of the critical points of iron and steel will not be without interest. In 1868 Tschernoff in studying the hardening of steel used the notation A for the temperature at which hardening by rapid cooling becomes suddenly possible in high carbon steel. This was the point $Ac_{3.2.1}$.

In 1869 Gore noted that at a dark red heat steel exhibited on cooling a spon-

taneous dilatation of short duration followed by normal contraction. Evidently the point of recalescence Ar_1 or $Ar_{3.2.1}$.

In 1873 Barrett repeated Gore's experiments and discovered, on heating, a momentary contraction at nearly the same temperature as the dilatation on cooling. This was the point Ac_1 or $Ac_{3.2.1}$. He further noted that this dilatation or contraction was very feeble in iron (the A_1 point in very low carbon steel) and very marked in hard steel (the point $A_{3.2.1}$). Barrett also discovered the spontaneous glow taking place on cooling a wire and gave it the name of "recalescence."

In 1879 Barrus showed that the increase of hardness resulting from quenching was not gradual but sudden, thus pointing to the existence of a thermal critical point (the A_1 point).

In 1885 Osmond published his discovery of the upper critical points A_3 and A_2 in iron and low carbon steel and gave the first accurate determination of the position of the point A_1 .

CHAPTER XI

THE THERMAL CRITICAL POINTS OF STEEL

THEIR CAUSES

The thermal critical points described in the preceding chapter are evidently outward manifestations of internal transformations taking place spontaneously at certain critical temperatures. We should now inquire into the nature of these transformations.

Let us remember that there are but three well-known causes of spontaneous evolutions of heat in cooling bodies and of spontaneous absorptions on heating. These are: (1) formation of chemical compounds, a phenomenon which is almost always accompanied by a spontaneous evolution of heat (the heat of formation), and the reverse phase, the dissociation of the compound with absorption of heat (the heat of dissociation), (2) changes of state, that is, the passage of a substance from the solid to the liquid or from the liquid to the gaseous state, or directly from the solid to the gaseous state, which changes are always accompanied by spontaneous absorptions of heat, and the opposite phases of the same phenomena, the passage of a body from the gaseous to the liquid or from the liquid to the solid state, when heat is evolved (the latent heat of solidification in case of a substance passing from the liquid to the solid state, etc.) these evolutions or absorptions of heat, as the case may be, maintaining the temperature of the substance constant while a change of state is in progress as, for instance, during solidification or melting, (3) allotropic or polymorphic transformations which are always accompanied by an evolution of heat when the body passes from one allotropic condition to another, and by an absorption of heat when it returns to its first allotropic form or vice versa. The meaning of allotropy has been discussed in Chapter V.

Causes of the Upper Points A_3 and A_2 in Carbonless Iron. — It has been seen that at these points spontaneous evolutions or absorptions of heat occur in chemically pure iron which, since they are not accompanied by any change of state (the metal being considerably below its solidification point) must, it seems, necessarily indicate the existence of iron under three allotropic forms. It has been mentioned in Chapter V that the allotropic form stable above A_3 is known as γ (gamma) iron, that stable between A_3 and A_2 as β (beta) iron, and the form stable below A_2 as α (alpha) iron. The following then takes place during the cooling and heating of pure iron: as the metal cools from a high temperature when the point Ar_3 is reached, it passes from the gamma to the beta condition with evolution of heat, while at Ar_2 it passes from the beta to the alpha form also with evolution of heat. On heating the reversals take place, the iron passing with absorptions of heat from the alpha to the beta condition at Ac_2 and from the beta to the gamma condition at Ac_3 . That the point A_3 indicates an allotropic transformation is universally admitted, no one doubting the

existence of iron in at least two allotropic conditions. Many authoritative writers believe with Osmond that the point A_2 also indicates an allotropic transformation, and that iron, therefore, assumes three distinct allotropic forms, as explained above. While some writers have expressed doubts as to the allotropic character of the point A_2 , as will presently be explained, in these pages iron will be assumed to exist in three allotropic conditions, of which A_3 and A_2 are the transformation points, this theory being, in the author's opinion, the one best supported.

The A_2 Point and Beta Iron. — The arguments which have been offered in support of the contention that the point A_2 of pure iron and of low carbon steel is not an allotropic point and that, consequently, beta iron does not exist, should be briefly considered.

(1) It was claimed by Benedicks and Carpenter that the point A_2 or at least Ac_2 does not occur in strictly pure iron, but in view of the results obtained by Dr. Burgess at the Bureau of Standards, and by others, the claim had to be withdrawn and the existence of A_2 as an independent point is no longer a debatable question.

(2) The point A_2 , it has been said, notably by Benedicks and H. Le Chatelier, cannot be an allotropic point because of the absence of hysteresis between the two phases Ac_2 and Ar_2 of the transformation. While it may be that hysteresis has always been observed in allotropic transformations, it does not by any means follow that its absence indicates the non-existence of allotropy. Indeed the freezing and melting of crystalline substances which may be considered as major instances of allotropy occur normally without hysteresis.

(3) The point A_2 , we are told, cannot be an allotropic point because no crystallographic change has ever been found to occur at that point. The argument is valid only in case it is accepted that an allotropic transformation necessarily implies a crystalline change, a definition of allotropy which is far from being generally entertained. It is quite possible, moreover, that a slight crystallographic change occurs at A_2 which has so far eluded observation.

(4) The absence of dilatation as iron cools through its Ar_2 point reported by some (Charpy and Grenet, and Benedicks) has been claimed to preclude the existence of allotropy. This argument is based on the arbitrary view that an allotropic transformation must necessarily be accompanied by dilatation on cooling and contraction on heating. Some investigators, moreover, believe to have detected a dilatation at Ar_2 , while even the results of Benedicks' careful experiments do not conclusively prove the absence of dilatation.

(5) While admitting that a marked transformation takes place at A_2 in the magnetic properties of iron, it has been argued that it was not of an allotropic character (H. Le Chatelier, Weiss, Honda, Benedicks, and others) (a) because it was not sufficiently sudden to imply discontinuity, and (b) because in general magnetic transformations of that kind are not allotropic. Ac_2 , we are told, marks the end of a progressive transformation having its starting point at a considerably lower temperature, while Ar_2 marks the beginning of the reverse change. Starting and end points of progressive transformations, however, are not accompanied by sudden evolution or absorption of heat; slight changes of direction only should occur in the thermal curves. While it is apparently true that the magnetic transformation starts at a temperature considerably below A_2 , the very existence of that point with its notable heat evolution indicates a sharp *discontinuity in the progressiveness* of the transformation and hence suggests allotropy; or, differently expressed, iron on being heated from

atmospheric temperature to just below its Ac_2 point loses *progressively* possibly 50 per cent of its ferro-magnetism, while in passing through its Ac_2 point it loses *abruptly* the remaining 50 per cent. It is unjustifiable to describe the phenomenon as merely a progressive transformation.

The recent theories put forward to show that the loss of ferro-magnetism suffered by some metals on being heated should not be regarded as allotropic transformations are purely arbitrary and speculative. It remains more consistent to regard the magnetic and non-magnetic conditions of the same substance as two allotropic states of that substance.

(6) It has been contended that no discontinuity in any of the properties of iron has ever been proved to take place at A_2 and that, therefore, the transformation cannot be an allotropic one. To this it may be answered (a) that the existence of a marked thermal critical point indicates a sharp discontinuity in the internal energy of iron, and that as an evidence of allotropy it is at least as conclusive as a discontinuity in any other property, (b) that discontinuity undoubtedly exists at A_2 in the magnetic properties of iron, and (c) that several investigators have noted a discontinuity in the dilatation of the metal (Rosenhain and Humfrey, although denied by others), in its tensile strength (Rosenhain and Humfrey), in its specific heat (Weiss and Beck, and Meuthen) and in its electrical resistance (G. K. Burgess and I. N. Kelberg). In regard to the latter property Burgess and Kelberg write:

"The exact determination of the variation of the electrical resistance of pure iron (99.98) in terms of temperature has been made over the range 0 to 950 deg. C., particular attention being given to the form of the curve over the A_2 and A_3 critical ranges . . . No anomalies are found in the resistance of iron until the A_2 region is approached, and at A_2 there is an inflection at 757 deg. C. in the resistance temperature curve shown as a sharp cusp in the temperature coefficient. At Ac_3 the resistance of iron falls abruptly by some 0.005 of its value, which is recovered within a 25 deg. interval, and above Ac_3 it increases greatly again. On cooling, the Ar_3 is accompanied by slight increases of resistance with falling temperature. Ac_3 and Ar_3 begin at the same temperature, 894 deg. C., and each extends over a temperature interval of 25 degrees. These resistance measurements show that A_2 is a strictly reversible transformation and A_3 is a transformation taking place at a higher temperature on heating than on cooling. These experiments are in agreement with the thermal observations previously recorded in Scientific Paper No. 213.

Whether or not either or both of these critical ranges A_2 and A_3 are to be considered allotropic points will depend upon the definition of allotropy, about which there does not appear to be agreement."

(7) To explain the existence of A_2 in impure iron without having recourse to allotropy, Benedicks attempted to show, through ingenious speculations, that the point Ar_2 indicated the end of the Ar_3 transformation, some gamma iron remaining untransformed below Ar_3 owing to the presence of impurities, the phenomenon being one of supercooling, and the resulting equilibrium therefore metastable. What had been hitherto called beta iron was in reality, then, a solid solution of gamma iron in alpha iron. As this highly speculative hypothesis demands the absence of A_2 (at least of Ac_2) in strictly pure iron, it may be considered as untenable. Benedicks, however, facing this difficulty attempted to explain that unless the cooling be very slow the point Ar_2 might still occur in pure iron without disproving his theory and likewise Ac_2 , on quick heating. He admits, however, that the intensity of A_2 should gradually

decrease as the purity of the iron increases. The facts are that both Ac_2 and Ar_2 occur sharply in the purest irons obtainable on very slow heating and cooling and that there are no indications of their decreasing in intensity in the purer metals. Benedicks' attempt to replace a theory simple in its conception and well supported by experimental evidences by a product of intellectual gymnastics has failed. Osmond's theory originated and grew in the laboratory, in close harmony with nature, while Benedicks' theory was evolved in the quiet of one's study.

From the foregoing considerations the following conclusions appear warranted: (1) A_2 is an independent thermal point and is a manifestation of a transformation taking place spontaneously in iron and low carbon steel, (2) A_2 can in no way be regarded as the end point or starting point of the A_3 transformation, and (3) whether A_2 marks or not an allotropic transformation depends on our definition of allotropy. If it be insisted that allotropy necessarily implies a change of crystalline forms, then it may be argued that A_2 is not an allotropic point. If, on the contrary, it is considered that a discontinuity in the internal energy of iron, made evident by spontaneous evolution or absorption of heat, is the criterion by which to judge of allotropy, then we are justified in believing in the existence of beta iron. This view is strengthened by the undoubted existence of a discontinuity in the magnetic properties of iron at the A_2 point, and of discontinuities observed by some investigators in other properties.

Causes of the Upper Critical Points A_3 and A_2 in Low Carbon Steel. — As might be expected the points A_3 and A_2 occurring in very low carbon steel also indicate allotropic changes in the metal. According to most writers, however, only that portion of the metal which at ordinary temperature exists as free ferrite is here affected. To make this matter clear it will be necessary to anticipate somewhat our subject while the diagram shown in Figure 179 will be useful.

In this diagram the three critical points of steel containing 0.20 per cent carbon, A_3 , A_2 , and A_1 as well as its solidification point and atmospheric temperature are represented by parallel lines drawn at suitable intervals in the scale of temperature. The metal is represented by the rectangular area $ABCD$. The diagram illustrates the following facts later to be discussed at greater length: (1) in the molten condition steel is considered to be a liquid solution of iron and carbon, (2) on reaching its solidification point the metal is converted into a solid solution of gamma iron and carbon known as austenite, (3) upon reaching Ar_3 some ferrite begins to be set free, (4) the ferrite as it is set free assumes the beta state, this liberation of ferrite and its allotropic transformation being probably one and the same phenomenon, (5) the formation of free ferrite continues as the steel cools from Ar_3 to Ar_1 , EFG representing the ferrite thus liberated, (6) on reaching the point Ar_2 the ferrite liberated between Ar_3 and Ar_2 , ML in the diagram, passes from the beta to the alpha condition. (7) the ferrite liberated between Ar_2 and Ar_1 , LNF in the diagram, assumes the alpha condition (according to some writers) without passing by the beta condition, while in the opinion of others the beta condition is assumed but is immediately followed by the alpha state, (8) while ferrite is being set free, the balance of the steel, $EKIF$, (according to most writers) preserves its condition of solid solution, gamma iron plus carbon, (9) upon reaching the point Ar_1 the residual solid solution, FI is converted bodily into pearlite, (10) from Ar_1 down to atmospheric temperature no further structural change takes place, the steel being finally made up of $BH = GF$ per cent ferrite and of $HC = FI$ per cent pearlite.

the beta condition. This diagram depicts accurately the generally accepted views in regard to the meaning of the critical points. If these views are correct several interesting inferences may be drawn as to the relative intensities of the critical points. The point A_3 in low carbon steel does not indicate a complete transformation, as too often loosely stated, but merely the *beginning*, at Ar_3 , or the *end*, at Ac_3 , of a transformation extending over a considerable range of temperature, i.e. from A_1 to A_3 . Theoretically, therefore, it would seem as if the point A_3 must correspond to a mere change of direction in cooling and heating curves rather than to well-marked jogs. The fact that a decided jog marks the point Ar_3 in very low carbon steel might be ascribed to hysteresis, the metal cooling to a temperature below that at which the A_3 change is due so that when the transformation begins to take place it does so with added intensity, hence the jog. The jog corresponding to the Ac_3 point of very low carbon steel is not so readily explained. But is not this jog much less pronounced than the one corresponding to Ar_3 ? The point Ar_2 marks (1) a complete transformation, namely, the passage from the beta to the alpha state of the free ferrite liberated between Ar_3 and Ar_2 and (2) the beginning of a transformation, namely, the passage to the alpha condition of the ferrite which continues to be liberated between Ar_2 and Ar_1 . Because of the complete transformation implied by the point A_2 we readily understand that it should correspond to a jog both in the heating and cooling curves, and since Ar_2 is due chiefly to the allotropic transformation of the ferrite liberated between Ar_3 and Ar_2 , we readily understand why it should occur at nearly the same temperature regardless of the carbon content. In the light of what precedes, however, the point A_3 in steel instead of being regarded as the manifestation of transformations occurring and completing themselves at a certain temperature, in reality indicates the *beginning* or *end* of transformations extending over a considerable range of temperature, namely, from A_3 to A_1 .

Cause of the Point $A_{3,2}$.—It has been seen that the point $A_{3,2}$ is apparently a merging of the points A_3 and A_2 of lower carbon steel and it seems natural to infer that the transformations which these points indicate, namely the two allotropic changes, are here likewise merged, that is, that they now take place at the same temperature. In other words that when the point $Ar_{3,2}$ is reached on cooling, the iron passes from the gamma to the beta and then immediately to the alpha state, the heat evolved being due to this double allotropic transformation. Some writers have claimed, however, that at the point $Ar_{3,2}$ the iron passes directly from the gamma to the alpha condition, the change of gamma to beta being suppressed in steel containing over 0.35 per cent carbon or thereabout. If such hypothesis were true it would have some important bearing upon the probable theory of the hardening of steel as explained in another chapter. In the author's opinion the more generally accepted view is better supported by experimental facts and other evidences and in these chapters the point $A_{3,2}$ will be considered as implying a double allotropic change. Most metallographists believe that like the independent points A_3 and A_2 the double point $A_{3,2}$ is the result of allotropic changes affecting the free ferrite only.

This setting free and allotropic transformation of ferrite is depicted diagrammatically in Figure 180 in the case of steel containing 0.60 per cent carbon and having, therefore, the two critical points $A_{3,2}$ and A_1 . *EGF* indicates the gradual liberation of ferrite and its conversion to the alpha state as the metal cools from $Ar_{3,2}$ to Ar_1 , the steel, after complete cooling, being made up of $BH = GF$ per cent ferrite and $HC = FI$ per cent pearlite.

If, as generally stated, the allotropic transformation of which $A_{3.2}$ is a manifestation affects only the free (pro-eutectoid) ferrite, the intensity of the point $A_{3.2}$ must decrease rapidly with decreasing pro-eutectoid ferrite, i.e. as the eutectoid composi-

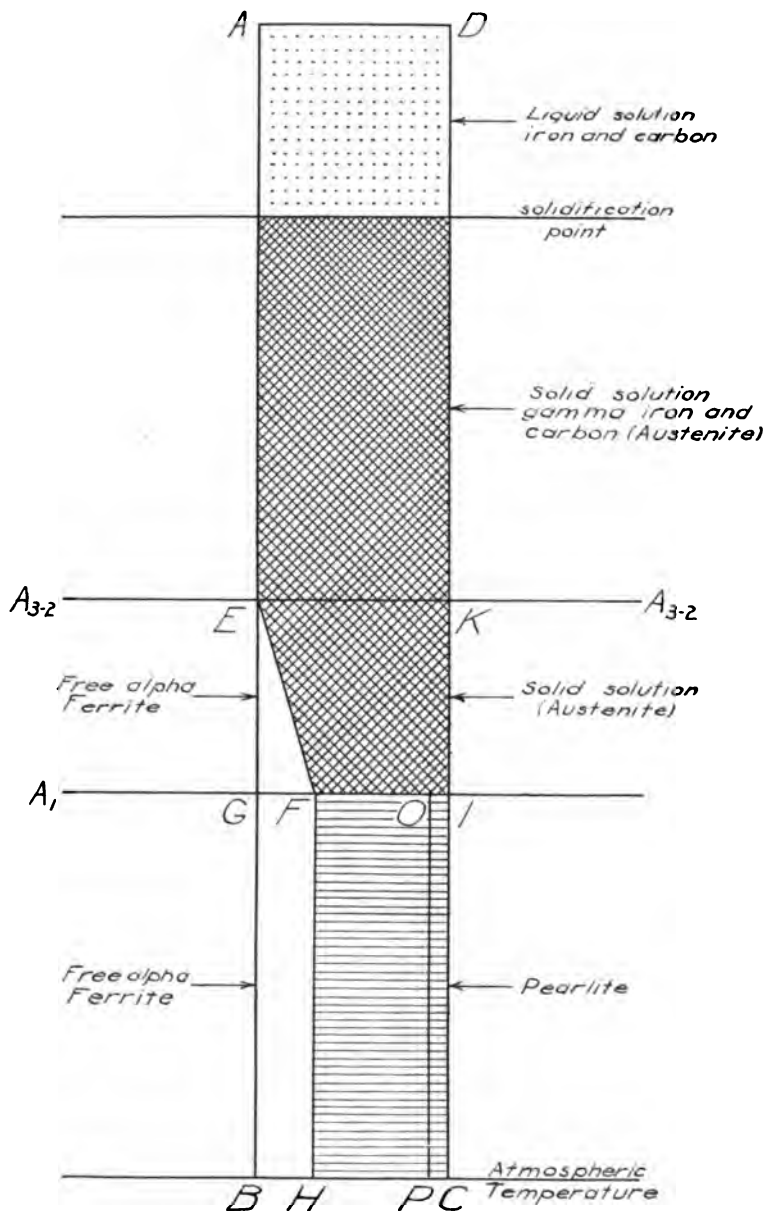
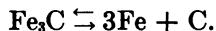


Fig. 180. — Diagram depicting structural changes in 0.60 per cent carbon steel as it cools slowly from the molten condition to atmospheric temperature.

tion is approached, and this point must vanish altogether as it meets the point A_1 (see Chapter X, Fig. 169), from which it further follows that the single point of eutectoid steel is not in reality a triple point as the notation $A_{3.2.1}$ would imply, resulting

from the merging of A_1 and $A_{3.2}$, but that on the contrary it remains a single point, being merely the continuation of the A_1 point of hypo-eutectoid steel.

Cause of the Point A_1 . — It has been seen that the point A_1 does not occur in carbonless iron, only feebly in iron containing little carbon, and with increased intensity as the carbon increases to the eutectoid point. The conclusion seems irresistible that the point A_1 must be closely related to the carbon, that it must indicate a sudden change in its condition. If steel be rapidly cooled from above the point Ac_1 and then treated with certain dilute acids, practically all the carbon escapes as hydrocarbons, whereas the same steel after slow cooling through Ar_1 when similarly treated yields a carbonaceous residue, which upon being analyzed is found to consist of the carbide Fe_3C . It is assumed that upon quick cooling we retain the carbon, partially at least, in the form in which it normally exists above A_1 , and seeing that when subjected to a similar treatment this carbon behaves so very differently from the carbon of slowly cooled steel, the conclusion is very logical that carbon exists above A_1 in a different condition from that normal below A_1 . Above A_1 it is called "hardening" carbon, below A_1 "cement" carbon. On heating steel past the point Ac_1 the carbon changes from the cement to the hardening condition, and vice versa on cooling at Ar_1 from the hardening to the cement condition. It is, moreover, generally believed that this hardening carbon is carbon in solid solution in the iron. If it be so the heat evolved at Ar_1 is clearly in part at least the heat of formation of the carbide Fe_3C and the heat absorbed at Ac_1 clearly the heat of dissociation of that carbide which now is resolved again into its elements according to the reversible reaction



The intensity of the A_1 point should then increase as the carbon increases or, rather, as the amount of pearlite increases, and should be maximum, therefore, at the eutectoid point as indicated in Figure 169, Chapter X. With higher carbon content it diminishes slightly because the free (pro-eutectoid) cementite which is now present takes no part in the transformation occurring at Ar_1 , having been formed at a higher temperature, namely, at Ar_{cm} , as later explained.

It would seem that the cause of the A_1 point, i.e. the point of recalescence, is in this way explained in a perfectly satisfactory manner. The correctness of this theory appears to be further supported by microscopical evidences which reveal the presence of Fe_3C in slowly cooled steel while pointing to the probable absence of it in suddenly cooled steel.

In recent years, however, it has seemed more and more probably to students of metallography that it is not carbon in its elementary state which is dissolved in iron at a high temperature, but rather the carbide Fe_3C itself and that the difference between the behavior of the carbon in hardened steel and in slowly cooled steel might well be satisfactorily accounted for on the ground that in hardened steel Fe_3C is *dissolved* in iron and in that form is much more readily acted upon by acids, being thereby converted into hydrocarbons, whereas Fe_3C when in the free crystallized condition, as in slowly cooled steel, resists the action of the acids and remains undissolved. If it is Fe_3C and not C which is dissolved in iron above the critical range, it is evident that the point Ar_1 cannot be caused by the *formation* of Fe_3C . But it may well be due to the crystallization or falling out of solution of Fe_3C . To be sure this is a falling out of a solid solution, but cannot we conceive that the falling out of a constituent of a solid solution is accompanied by an evolution of heat even if it does not

imply a change of state? In other words is it not possible, or even probable, that crystallization in the solid state is accompanied by an evolution of heat? Surely this crystallization implies an allotropic or at least a polymorphic transformation and are not such transformations always accompanied by heat evolutions?

The author offers these thoughts as possibly worthy of attention and as a possible explanation of the evolution of heat at Ar_1 if we assume that Fe_3C and not C , as it now seems so probable, is dissolved in iron above that point.

The Point A_1 an Allotropic Point. — Most writers describe the point A_1 as purely a carbon point, that is, a manifestation of a change affecting the condition of the carbon only as explained in the foregoing pages. These same writers, however, assert that the upper critical points, A_3 and A_2 in low carbon steel or $A_{3.2}$ in higher carbon steel, affect only the condition of the free (pro-eutectoid) ferrite. In this they are inconsistent, for if the upper point or points indicate allotropic transformation of the free ferrite only then the lower point A_1 is decidedly an allotropic point seeing that it corresponds to allotropic transformations of the pearlite-ferrite and that in steel containing more than some 0.40 per cent carbon there is more pearlite-ferrite than free ferrite. In other words the point A_1 is always an allotropic point indicating an allotropic transformation of the pearlite-ferrite similar to the allotropic transformation of the free ferrite occurring at the upper points, and in case of steel with more than 0.40 per cent carbon the allotropic change taking place at A_1 affects a larger bulk of iron than the change at $A_{3.2}$. To make the matter clear let us consider (Fig. 180) a steel containing some 0.60 per cent of carbon and, therefore, made up after slow cooling of 72 per cent of pearlite and 28 per cent of free ferrite. This steel will contain about $72 \times \frac{7}{8} = 63$ per cent of pearlite-ferrite represented by FO in Figure 180. When the point A_1 is reached this 63 per cent of iron is still in the gamma condition (according to the general belief) and now passes to the alpha condition either directly or first assuming the beta state. The allotropic character of the point A_1 is therefore evident. Indeed it is sufficient to account for the heat evolved at Ar_1 or absorbed at Ac_1 without the assistance of any change occurring in the carbon condition, for it is in perfect agreement with the increased intensity of the point A_1 as the carbon increases and with its maximum at the eutectoid composition, since as the carbon increases the amount of pearlite and therefore of pearlite-ferrite likewise increases.

Summing up, three reasons may be given for the evolution of heat at Ar_1 : (1) formation of the carbide Fe_3C based on the assumption that carbon as such is dissolved in iron, (2) crystallization of the carbide Fe_3C based on the assumption that this carbide is dissolved in iron and that crystallization not implying a change of state may produce heat, and (3) allotropic transformation of the iron present in austenite of eutectoid composition. It seems probable that both (2) and (3) contribute to the heat developed at Ar_1 .

Pearlite Formation. — Whatever differences of opinion may exist as to the exact cause or causes of the evolution of heat corresponding to the point Ar_1 all agree that it is due to the transformation of austenite of eutectoid composition (sometimes called hardenite) into pearlite, i.e. the conversion of a solid solution into an aggregate (ferrite plus cementite). It is well to bear in mind the changes in the condition of the iron and carbon which this transformation seems to imply: (1) passage of the iron from the gamma to the beta condition, (2) immediately followed by its conversion into alpha iron or, according to some writers, (1 and 2) the conversion of gamma

iron directly into alpha iron, skipping the beta state, (3) the crystallizing of alpha iron into parallel plates or lamellæ, and (4a) the formation and crystallizing, or (4b) the crystallizing only of Fe_3C into parallel plates alternating with the ferrite plates.

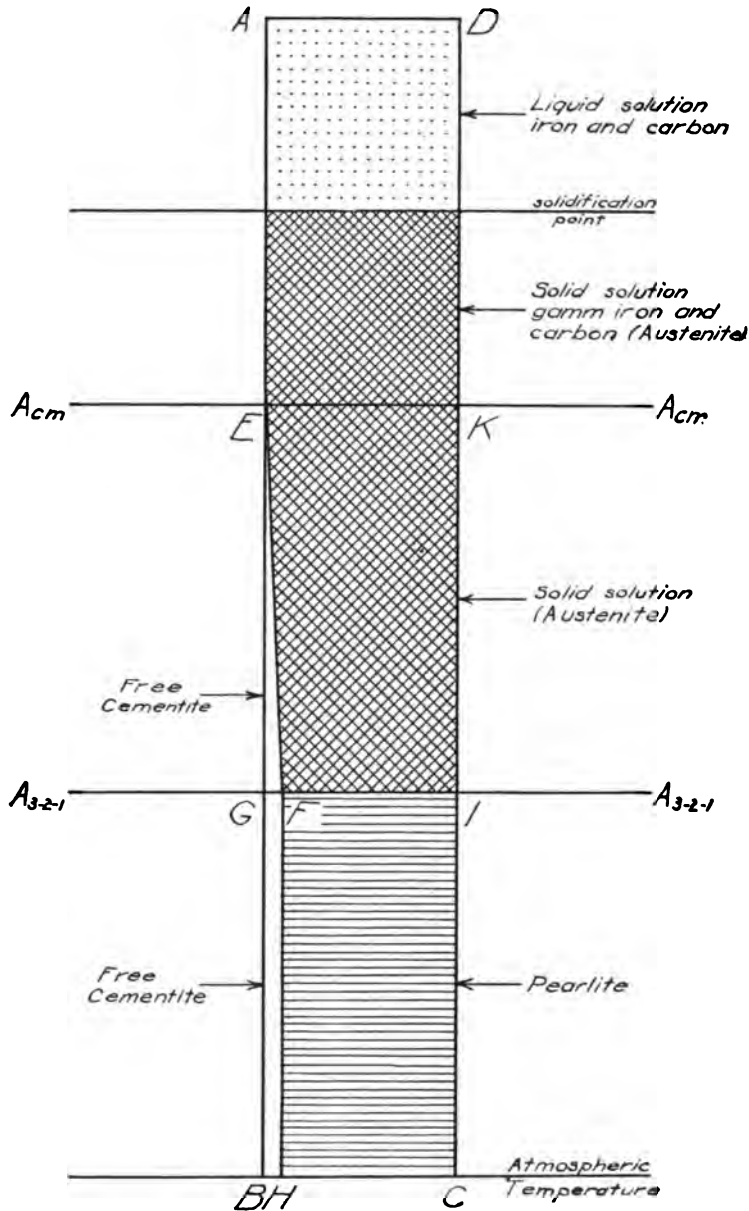


Fig. 181. — Diagram depicting structural changes in 1.25 per cent carbon steel as it cools slowly from the molten condition to atmospheric temperature.

Cause of the Point A_{cm} . — The point A_{cm} undoubtedly indicates the beginning of the liberation of free cementite in hyper-eutectoid steel as it cools from A_{cm} to A_{3-2-1} . This gradual formation of free cementite is well shown in Figure 181 where it

is represented by the triangle *EFG*. When the point $Ar_{3.2.1}$ is reached the residual austenite, now of eutectoid composition, is converted bodily into pearlite, the steel consisting finally of $BH = GF$ per cent free cementite and $HC = FI$ per cent pearlite. It will be seen that this upper point of hyper-eutectoid steel, like the points A_1 and A_2 of hypo-eutectoid steel, does not indicate a complete transformation but merely the beginning of a transformation covering a wide range of temperature, namely, from A_{cm} to $A_{3.2.1}$. If it corresponds to a jog rather than to a mere change of direction in cooling curves this must be ascribed to hysteresis and its tendency to accentuate the beginning of a transformation as previously explained. The evolution of heat corresponding to the liberation of free cementite may be explained in two ways: (1) actual formation of Fe_3C , carbon and not the carbide being in solution above Ar_{cm} or (2) crystallization or falling out of solution of Fe_3C based on the more probable assumption that Fe_3C and not C is dissolved by the iron above Ar_{cm} , and on the further assumption that this crystallization in the solid state, since it evidently implies an allotropic or, at least, polymorphic change, must be accompanied by an evolution of heat.

Since in hyper-eutectoid steel containing even as much as 1.5 per cent carbon there is but a small proportion of free cementite (some 11 per cent) the point Ar_{cm} is caused by the evolution of but a small amount of heat and must therefore be faint. Its intensity, moreover, must decrease as the carbon decreases and the point must disappear altogether as the eutectoid composition is reached, that is, just as it meets the single point of eutectoid steel. This is indicated in Figure 169 of Chapter X.

Allotropy of Cementite.—If we believe, as most metallographists now do, that Fe_3C and not C forms a solid solution with iron above the point A_1 or $A_{3.2.1}$, it follows that this dissolved Fe_3C crystallizes or falls out of solution at certain critical temperatures, namely, Ar_{cm} for the free cementite of hyper-eutectoid steel and Ar_1 (or $Ar_{3.2.1}$) for the pearlite-cementite of all steels, and that this crystallization is accompanied by an evolution of heat. This falling out of solution really implies a spontaneous change of crystalline form and is therefore an evidence of polymorphism, hence of allotropy, for if allotropy does not necessarily imply polymorphism, polymorphism implies allotropy. Are we not then justified in believing that Fe_3C may exist under two allotropic forms: (1) an allotropic variety soluble in iron, which we may call gamma cementite and (2) an allotropic variety insoluble in iron, which we may call alpha cementite, constituting the free cementite of hyper-eutectoid steel and the hard plates of pearlite.

The fact that the crystallizing or falling out of solution of free ferrite in hypo-eutectoid steel implies an allotropic transformation of the liberated ferrite, points with force to a similar transformation forming part of the liberation of free cementite in hyper-eutectoid steel. In the case of iron we are able actually to prove this allotropy through the cooling of very pure iron and the testing of its properties while in the case of cementite such direct proof is not yet at hand because of the difficulty of obtaining pure cementite and of testing it after producing it.

To generalize, it would seem as if the crystallizing or falling out of solution of a substance at certain critical temperatures always implies a spontaneous change of crystalline form and, therefore, an allotropic transformation of the substance separating from the solution, whether that solution be liquid or solid. In the former case the falling out of solution implies a change of state, the separating substance passing from the liquid to the solid state, but does it make it less of an allotropic change?

Allotropic transformations which also imply changes of state might be called instances of major allotropy to distinguish them from those instances in which changes of internal energy are not accompanied by changes of state.

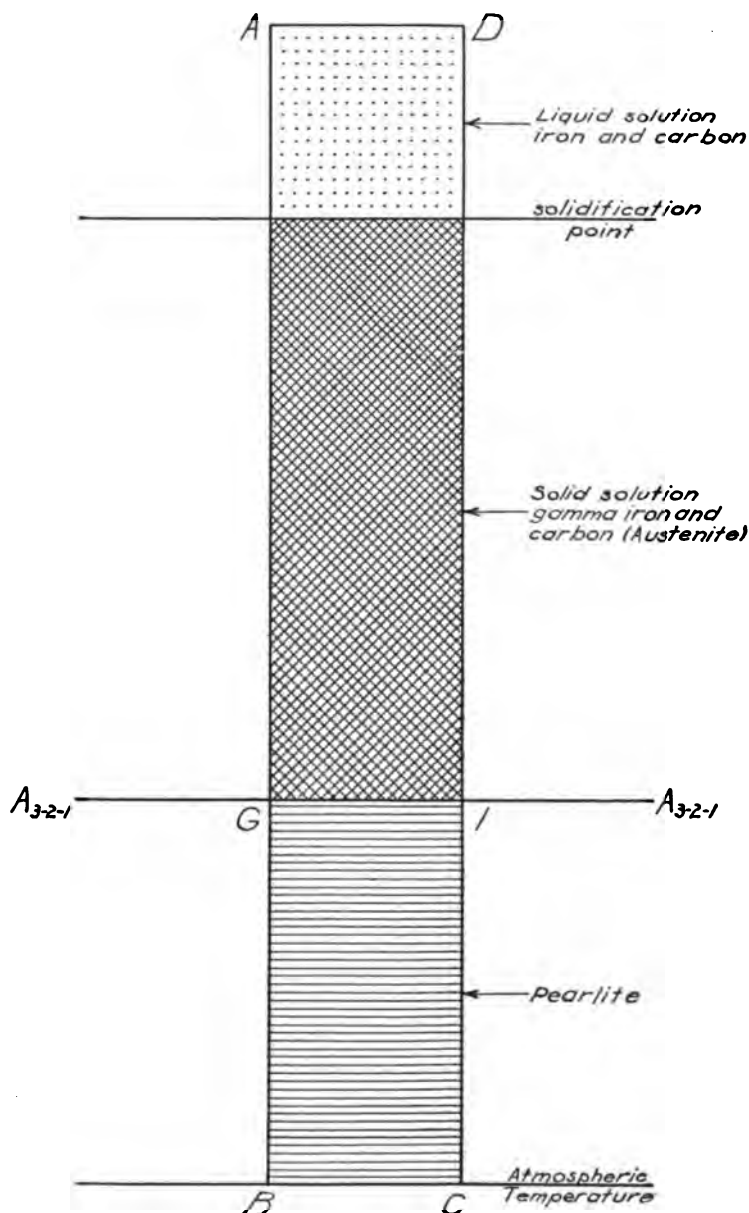


Fig. 182. — Diagram depicting structural changes in eutectoid steel as it cools slowly from the molten condition to atmospheric temperature.

Cause of the Point A_{3-2-1} in Eutectoid Steel. — In the case of eutectoid steel the solid solution (austenite) is originally of eutectoid composition and, therefore, on cooling reaches the point A_{3-2-1} without rejecting either ferrite or cementite, hence

the absence of upper points in eutectoid steel. On passing through the point $Ar_{3.2.1}$ (Fig. 182) this austenite is converted into pearlite. Pearlite contains 87.50 per cent of ferrite which undergoes allotropic transformation at $Ar_{3.2.1}$, hence the intense allotropic character of this point. The crystallizing of cementite probably contributes also to the heat evolved at $Ar_{3.2.1}$ whether it implies the *formation* of Fe_3C or not as explained before. It has also been argued that this crystallizing of cementite probably implies an allotropic transformation, in which case the point $A_{3.2.1}$ (and A_1 as well) would be solely an allotropic point, resulting from the simultaneous allotropic transformation of both the iron and the Fe_3C of austenite of eutectoid composition.

Finally let us bear in mind that notwithstanding its notation the single point of eutectoid steel does not in fact result from the merging of the several points of hypo-eutectoid steel, being merely a continuation of the point A_1 . This point A_1 is essentially a "pearlite" point while the upper points of hypo-eutectoid steel are "ferrite" points and the upper point of hyper-eutectoid steel is a "cementite" point.

Cause of the Point $A_{3.2.1}$ in Hyper-Eutectoid Steel. — The point $A_{3.2.1}$ in hyper-eutectoid steel is of exactly the same nature as the point $A_{3.2.1}$ of eutectoid steel and the point A_1 of hypo-eutectoid steel. It marks the formation of pearlite, bearing in mind the various changes in the condition of the carbon and iron implied by that formation. As the proportion of pearlite now decreases with increase of carbon the intensity of the point $A_{3.2.1}$ likewise diminishes.

Summary. — The apparent causes of the thermal critical points of iron and steel may be briefly summed up as follows:

The point Ar_3 of carbonless iron and of steel containing less than some 0.35 per cent carbon marks the beginning of the liberation of ferrite (which liberation continues down to the point Ar_1) and the transformation of that ferrite from the gamma to the beta condition, this setting free of ferrite and its allotropic transformation being probably simultaneous.

The point Ar_2 of carbonless iron and of steel containing less than some 0.35 per cent carbon indicates the transformation from the beta to the alpha condition of the ferrite liberated between Ar_3 and Ar_2 and the beginning of the passage of the ferrite, which continues to be liberated as the metal comes from Ar_2 to Ar_1 , from the gamma to the beta and then to the alpha condition or, as some writers claim, directly from the gamma to the alpha state.

The point $Ar_{3.2}$ of steel containing somewhere between 0.35 and 0.85 per cent carbon marks the beginning of the liberation of ferrite which takes place between $Ar_{3.2}$ and Ar_1 and the passage of that ferrite from the gamma to the beta condition and immediately to the alpha state or, according to some writers, directly from the gamma to the alpha condition.

Since only the formation and transformation of free ferrite is involved at the points A_3 , A_2 , and $A_{3.2}$, these points may properly be called "ferrite" points.

The point A_1 of hypo-eutectoid steel, as well as the point $A_{3.2.1}$ of eutectoid and hyper-eutectoid steel, marks the rather sudden transformation of the residual solid solution (austenite), now of eutectoid composition, into pearlite, bearing in mind the changes in the conditions of the iron and carbon which such transformation implies. The points A_1 and $A_{3.2.1}$ may properly be called "pearlite" points.

The point Ar_{cm} of hyper-eutectoid steel marks the beginning of the setting free of cementite as the metal cools from Ar_{cm} to $Ar_{3.2.1}$, the liberation of cementite probably involving an allotropic change of that constituent as previously explained.

In Figure 183 an attempt has been made at showing diagrammatically the relation between the critical points of steel and its structural composition after slow cooling. It will be readily understood. The upper part of the diagram shows the location of the critical points, the lower part the structural composition in percentages of ferrite, pearlite, and cementite. Taking, for instance, a steel containing 0.25 per cent carbon: above A_3 at A it is a solid solution of carbon and iron (austenite); on cooling through Ar_3 at B some beta ferrite is set free, this liberation continuing from B to C ; on cooling through Ar_2 at C the free beta ferrite is converted into alpha ferrite while additional alpha ferrite forms as the metal cools to Ar_1 , that is from C to D . The ferrite liberated on cooling from B to D , that is on cooling through the critical range, is represented in the lower part of the diagram by DE which is also the final percentage of free ferrite in the steel. As the metal cools through its Ar_1 point

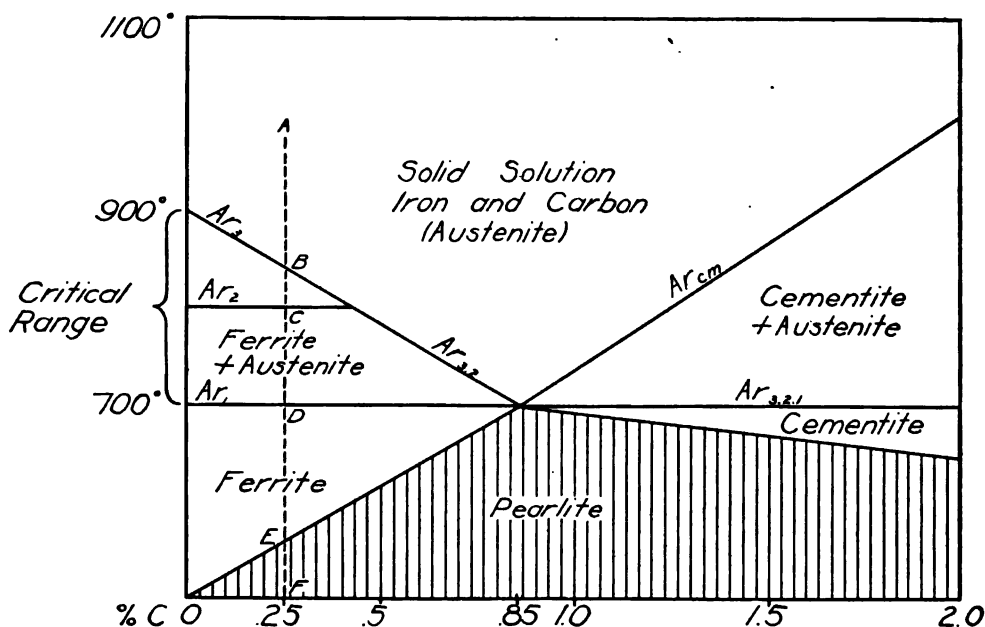


Fig. 183. — Diagram showing the relation between the critical points and the structural composition of slowly cooled steel.

at D , the residual austenite, at present of eutectoid composition, is converted into pearlite, EF representing the pearlite here formed, i.e. the percentage of pearlite in the steel. The structural formation of any steel can be followed in the same way in this diagram. It will be obvious that the vertical distances representing the percentages of ferrite, pearlite, or cementite in any steel may also be regarded as proportional to the intensities of the corresponding critical points. For instance, the distance ED may be assumed to be proportional to the combined intensities of the points Ar_3 and Ar_2 of a 0.25 per cent carbon steel and the distance EF proportional to the intensity of the A_1 point. Interpreted in this way the diagram indicates what has already been pointed out: (1) that the intensities of A_3 and A_2 decrease as the carbon increases, these points vanishing on reaching the eutectoid composition, (2)

that the point A_1 , very faint at first, increases rapidly with increased carbon, becoming maximum at the eutectoid point and then decreasing, and (3) that the point A_{cm} , always faint, increases slightly as the carbon increases above 0.85 per cent.

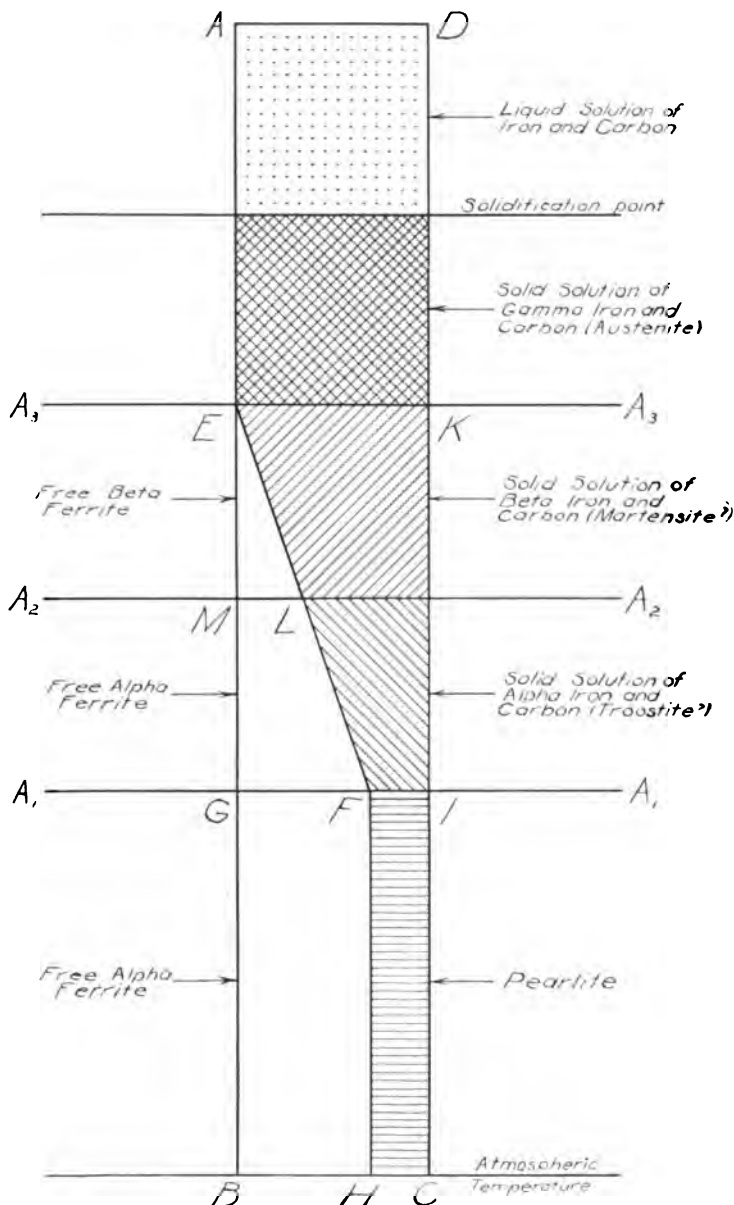


Fig. 184. — Diagram depicting structural changes in 0.20 per cent carbon steel slowly cooled, assuming that the iron remaining in solution as well as the free iron (ferrite) undergoes allotropic changes. To be compared with Figure 179.

Another View of the Allotropic Changes. — It will be obvious from the description of the underlying causes of the critical points given in the foregoing pages that, according to the general belief, iron must first be freed from solid solution before it can undergo any allotropic changes or, at

least, its liberation from solution and its allotropic transformation take place simultaneously, the latter never preceding the former. In 1906 the author expressed the opinion that it was far from certain that its liberation from solution must precede, or at least be simultaneous with, the allotropic changes affecting iron at certain critical temperatures. He ventured to put forward, in a tentative

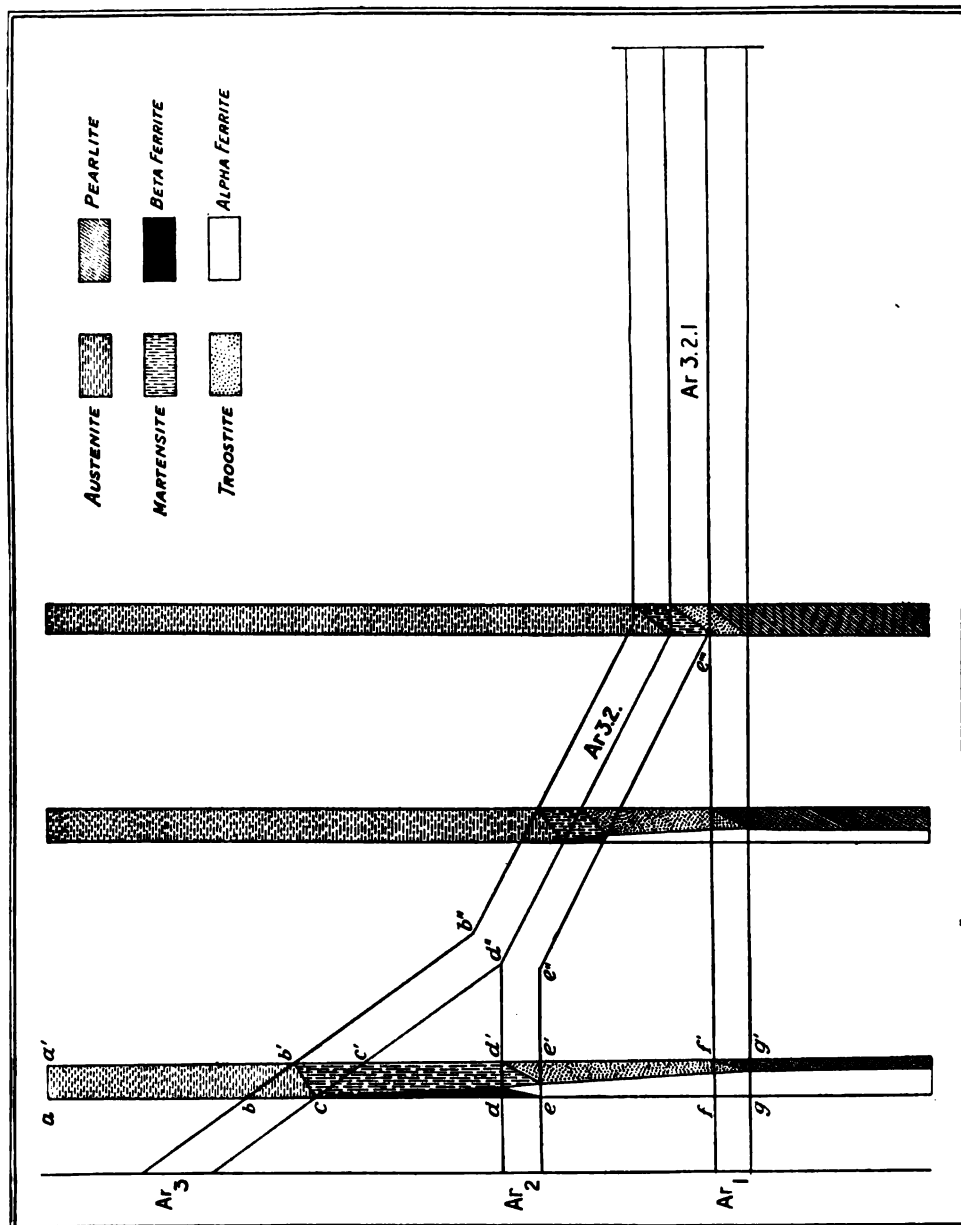


Fig. 185.

way, the hypothesis that iron in solution might first undergo an allotropic transformation and then be expelled in its new allotropic form. This view was not favorably received but, as it has not been shown to be by any means untenable, the author still believes it worthy of record in these pages. It is evident that if the allotropic transformation of iron from the gamma to the beta and then to the

alpha state precedes its liberation from solution, three solid solutions of carbon in iron are formed during the slow cooling of steel, namely, carbon (or the carbide Fe_3C) dissolved (1) in gamma iron, (2) in beta iron, and (3) in alpha iron. The first solid solution is universally called austenite while the hypothesis leads almost irresistibly to regarding the solid solution in beta iron as martensite and the solid solution in alpha iron as troostite, two constituents to be described later.

With the assistance of the diagram, Figure 184, and by comparing it with Figure 179 the working of the present hypothesis will be readily understood. In Figure 184 are depicted the structural changes taking place during the slow cooling of steel containing 0.20 per cent carbon and therefore exhibiting the three critical points A_3 , A_2 , and A_1 . On cooling through the point A_3 the solid solution of carbon and gamma iron (austenite) existing above A_3 is converted into a solid solution of carbon in beta iron (martensite?). In the beta condition, however, iron cannot be retained in solution and begins immediately to be liberated, and its liberation continues as the metal cools down to A_2 . Between A_2 and A_1 we have a solid solution of beta iron decreasing in amount and increasing free beta ferrite. On cooling through A_1 both the free beta ferrite and the dissolved beta ferrite pass to the alpha state, giving rise to the formation of free alpha ferrite and of a solution of carbon in alpha iron (troostite?). On cooling from A_1 to A_1 additional alpha ferrite is liberated while the proportion of carbon-alpha iron solution decreases correspondingly. At A_1 the remaining solution has become of eutectoid composition and is converted bodily into pearlite, the mechanism of this transformation being well understood. It will be evident that in the case of hypo-eutectoid steel having but one upper critical point, $A_{3,2}$, in cooling through that point the metal would pass from the condition of a solid solution of carbon in gamma iron to that of a solid solution in beta iron and then immediately to that of a solid solution in alpha iron, the steel between $A_{3,2}$ and A_1 being composed of this solution in alpha iron (troostite?) and of free alpha ferrite. With eutectoid steel the following changes would take place as it cools through its single critical point $A_{3,2,1}$: (1) transformation of gamma iron solid solution (austenite) into beta iron solid solution (martensite?), (2) immediately followed by the formation of alpha iron solid solution (troostite?), (3) immediately followed by formation of pearlite.

The author thinks that the decreasing intensities of the points A_3 and A_2 as the carbon content increases is the fact most difficult to reconcile with the hypothesis just outlined, for if these points are due to allotropic transformations affecting the entire bulk of the steel their intensities should be quite independent of the amount of carbon present. To be sure, this gradual diminution of the magnitude of the points A_3 and A_2 as the carbon increases is likewise difficult of explanation in the light of the universally accepted hypothesis that free iron only can be allotropically transformed, for it has been made clear in the foregoing pages that these points must indicate then the *beginnings* of transformations and not transformations carried to completion at those critical points, so that the intensities of the points should be little affected by the magnitude of the transformations themselves, that is, by the amount of free ferrite undergoing allotropic transformation or, which is the same thing, by the percentage of carbon in the steel.

The view just outlined as to the mechanisms of the allotropic changes is further depicted diagrammatically in Figure 185, in which the critical points are represented as covering certain ranges of temperature making it possible to show, graphically, the changes taking place within these ranges. Taking an iron-carbon alloy having, for instance, the composition a (some 0.20 per cent carbon), the diagram shows that above A_3 it is made up of aa' , i.e. of 100 per cent austenite; on cooling through A_3 it is gradually converted into martensite; between A_3 and A_2 beta ferrite is liberated; in passing through A_2 the remaining martensite is gradually converted into a solid solution of carbon and alpha iron (troostite?) while the free beta ferrite is converted into free alpha ferrite; between A_2 and A_1 additional alpha ferrite is liberated; in cooling through A_1 the remaining solid solution (troostite?), now of eutectoid composition, is converted into pearlite. The structural changes occurring in steel having but one upper critical point and in steel of eutectoid composition are similarly depicted. This diagram is reproduced from the "Journal of the Iron and Steel Institute," No. IV, for 1906, Plate LII.

CHAPTER XII

THE THERMAL CRITICAL POINTS OF IRON AND STEEL

THEIR EFFECTS

It has been shown in preceding chapters that the thermal critical points of iron and steel are due chiefly if not wholly to allotropic transformations of the iron. It is a well-known fact that when a substance undergoes an allotropic transformation many of its properties undergo likewise deep and sudden changes at the critical temperatures. Color, crystallization, dilatation, conductivity both for heat and electricity, strength, ductility, hardness, specific gravity are properties frequently affected as a body passes from one allotropic form to another. We should expect, therefore, such changes to take place, as iron undergoes its allotropic transformations, if not in all, at least in some of the above properties. And it is because such changes do take place that a clear understanding of the occurrence and significance of the critical points is of much practical importance to the iron and steel metallurgist.

CHANGES AT A_3

It has been shown that the point A_3 occurs in carbonless iron and in steel containing less than some 0.35 per cent of carbon and that it is universally believed that this point indicates an allotropic change, the iron passing from the gamma to the beta condition, or according to some to the alpha condition, on cooling at Ar_3 , and vice versa, from the beta (or alpha) to the gamma condition on heating at Ac_3 . It should be borne in mind, however, as fully explained in Chapter XI that the general belief is that free ferrite only undergoes this change. As the metal cools past its point Ar_3 the following abrupt changes in some of its properties have been noted.

Dilatation. — The metal, which above the point Ar_3 was contracting, as is the general rule with all cooling bodies, on passing through the point Ar_3 undergoes suddenly a marked dilatation, amounting to over $\frac{1}{1000}$ of its length, immediately followed again by a normal contraction. Such dilatation implies that the change of gamma into beta iron takes place with augmentation of volume, or in other words that gamma iron is denser, has a higher specific gravity than beta iron. The dilatations occurring at Ar_3 in the case of steels containing respectively 0.05 and 0.15 per cent carbon are shown graphically in Figure 186. On heating, at Ac_3 a spontaneous contraction occurs of the same magnitude as the dilatation on cooling. Benedicks determined with great care the dilatation of pure iron between 700 and 950 deg. C. and some of his results are shown in Figure 187. The sharp occurrence of a marked dilatation at C , the A_3 point, will be noted. Had we no other evidence of an allotropic transformation at this critical temperature, this sudden dilatation taking place as it does in pure iron would justify our belief in its existence.

Electrical Conductivity. — Above the point A_3 the metal has an electrical resistance some ten times greater than its resistance at ordinary temperature. As it cools from a high temperature to the point A_3 , there is but a feeble decrease of its electrical resistance, but as soon as A_3 is reached it begins abruptly and sharply to decrease and keeps on decreasing at a normal rate to atmospheric temperature. At A_3 , therefore, we have a sudden and marked change in the variation of the electrical conductivity corresponding to a sharp break in the curve expressing the relation between temperature and electrical resistance as shown in Figure 188. On heating, at A_3 , the opposite change takes place, that is, the electrical resistance quite suddenly ceases to

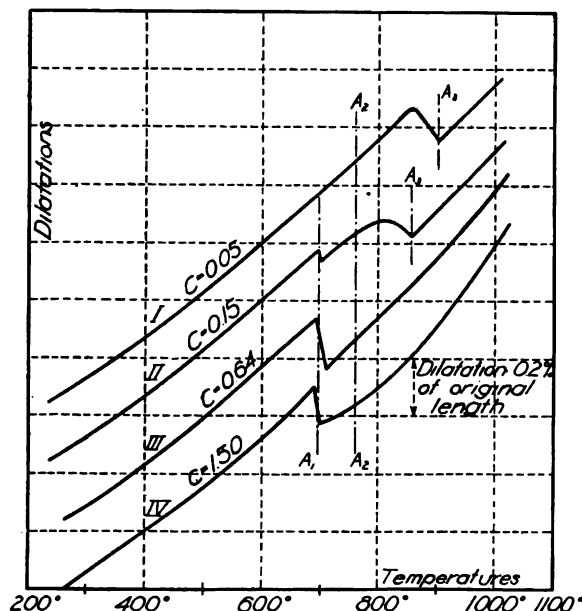


Fig. 186. — Dilatation curves of various carbon steels.

increase. So marked and sudden a change in a physical property is in itself a proof of an allotropic transformation.

Crystallization. — It has been shown in Chapter V that while gamma and beta iron both crystallize in the cubic system (Osmond) octahedra are the prevailing form of gamma iron while the cube is the crystalline form of beta iron, and that the transformation of gamma into beta iron includes a change in the planes of symmetry, at least of carburized iron (Osmond).

Tensile Strength. — Rosenhain and Humfrey have shown the existence of a distinct discontinuity in the tensile strength of iron at the A_3 point.

Dissolving Power for Carbon. — Above the point A_3 iron possesses dissolving power for carbon, while according to some writers it loses that power on passing through A_3 ; in other words gamma iron can dissolve carbon but beta iron is deprived of that power. It does not, however, seem, by any means, proven that beta iron cannot dissolve carbon, many authoritative workers holding the opposite view. This question will be discussed at greater length in another chapter.

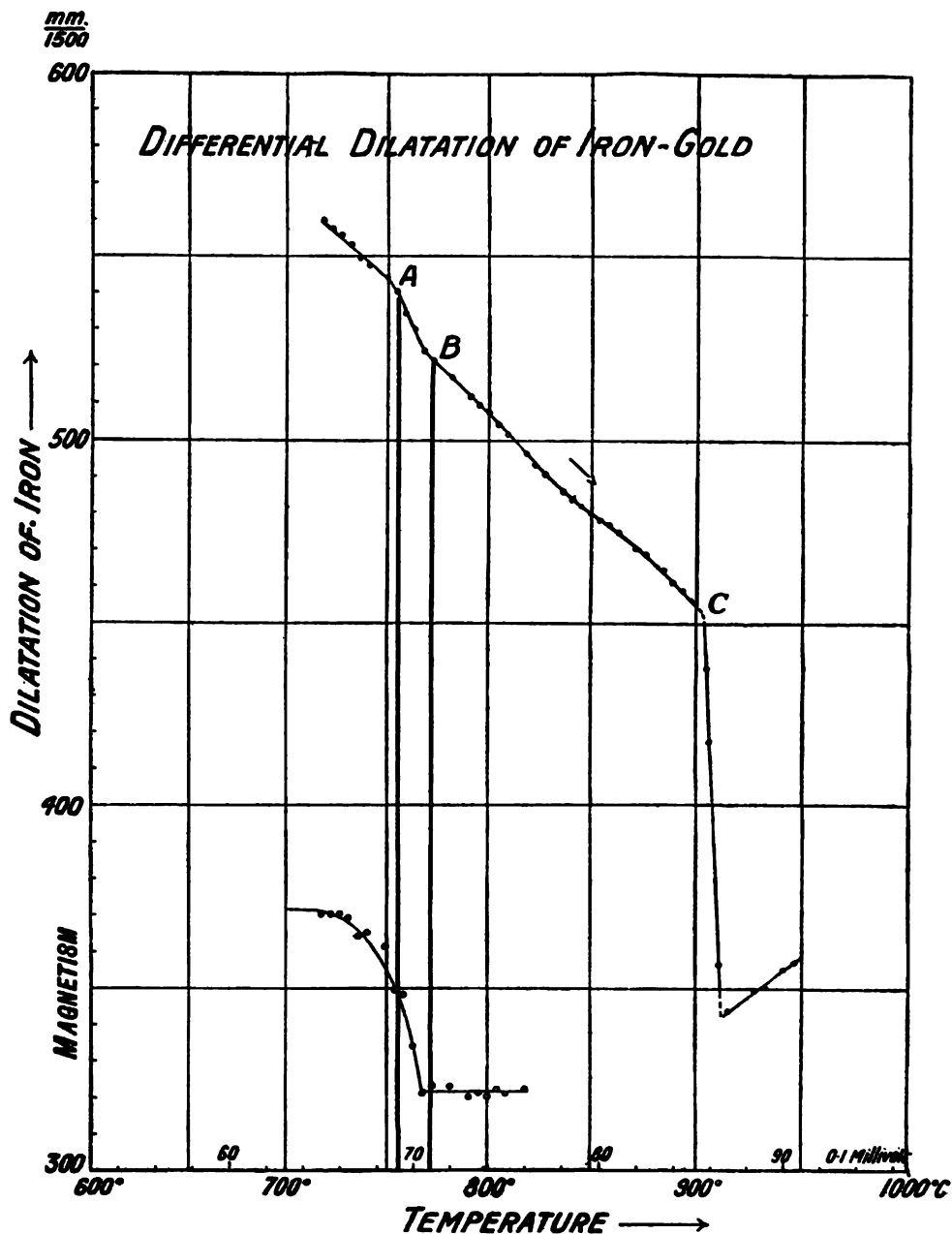


Fig. 187. — Dilatation of pure iron. (Benedicks.)

Structural Properties. — It has been explained at length in Chapter XI that the point A_{r3} corresponds to an abrupt structural change, namely, the beginning of the setting free of ferrite (Fig. 179, Chapter XI).

Other Properties. — Le Chatelier mentions a change in the variation of the thermo-electric force and a sudden but slight variation in magnetic properties as

taking place at A_3 . Meuthen reports a discontinuity in the specific heat of iron between 880 and 900 deg. C., that is at the A_3 point.

CHANGES AT A_2

As a separate point A_2 occurs in carbonless iron and in steel containing less than some 0.35 per cent of carbon. The changes of properties taking place at A_2 are not generally as abrupt nor are they as marked as those occurring at the other critical points. It is precisely because of this lack of sharpness and suddenness that some metallographists have questioned the accuracy of the view that this point like A_3 indicates an allotropic transformation. Careful consideration of the evidences at hand appear to show, however, that changes of properties do occur at A_2 sufficiently marked and sudden to warrant the classification of this point as an allotropic one. The fact that these changes are more gradual than at the other critical points is

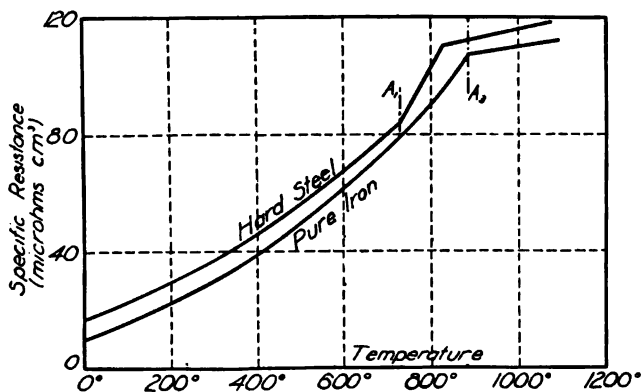


Fig. 188. — Electrical resistance curves of iron and high carbon steel.

logically explained by Osmond on the ground that beta and alpha iron are isomorphous, that is, capable of forming solid solutions and that therefore the passage of one variety into the other must necessarily be gradual as well as the variations of the properties of iron which the transformation implies.

Dilatation. — According to Le Chatelier, to Charpy and Grenet, to Benedicks, and others, no dilatation takes place as the metal cools past the point Ar_2 and they see in this an indication that A_2 is not an allotropic point. Osmond's reply is that the curves obtained by Charpy and Grenet, for instance, do indicate a dilatation at Ar_2 which, however, the authors fail to notice because the transformation not being sudden the dilatation likewise is gradual, whereas the authors were looking for sudden dilatations only. Some of Benedicks' careful measurements of the dilatation of pure iron are shown graphically in Figure 187. The contraction observed on heating, between A and B , that is during the A_2 range is described by him as a "slight, fully continuously occurring contraction (under heating) which entirely coincides with the gradual disappearance of the ferro-magnetism." Considering, however, that the striction which clearly reveals the position of A_2 covers a range of temperature not exceeding some 15 deg., it seems to point to a discontinuity in the dilatation of the metal rather than to a perfectly progressive transformation.

Magnetic Properties. — Above the point A_2 steel is non-magnetic, it is not attracted by a magnet, but in passing through Ar_2 it suddenly becomes strongly magnetic. Or, to use physicists terms, above A_2 iron is para-magnetic, below A_2 it is ferro-magnetic. Is not this abrupt and momentous change alone, in the magnetic properties of a metal, sufficient proof of an allotropic transformation? It is true that magnetism is not *fully* regained until a considerably lower temperature is reached, probably some 550 deg. C., according to Osmond, but the fact remains that the *greatest part* of the final magnetism of the metal is *abruptly* acquired as it cools past the point A_2 . What transformation other than an allotropic one can satisfactorily account for this?

The relation between the carbon content of steel and the temperatures at which the metal loses its magnetism on heating and regains it on cooling is shown graphically in Figure 189. The points plotted in this diagram represent the average values of a great number of determinations made by Madame Sklodowska Curie with a series of

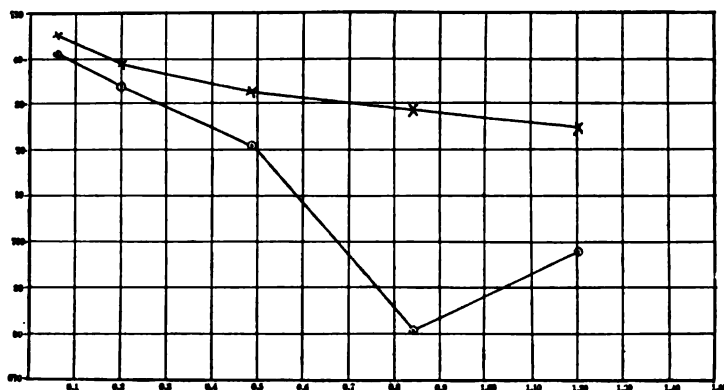


Fig. 189. — Temperatures of magnetic transformations of various carbon steels.

very pure carbon steels. It will be noticed that the points of magnetic changes correspond closely to the thermal critical points A_2 , $A_{3.2}$, or $A_{3.2.1}$. With little carbon there is but a small gap between the appearance of magnetism on cooling and its disappearance on heating, because the points Ar_2 and Ac_2 occur at nearly the same temperature; with 0.50 per cent carbon the magnetic points are lowered and so, likewise, the point $A_{3.2}$ while the gap increases, this being consistent with the greater gap between $Ar_{3.2}$ and $Ac_{3.2}$; with 0.84 per cent carbon the magnetic points are further lowered and the gap between them increased still more, this being in harmony with the location of the point $A_{3.2.1}$ which is lower than $A_{3.2}$ and with the greater gap between $Ar_{3.2.1}$ and $Ac_{3.2.1}$.

Further experimental evidences that the points of magnetic transformations coincide with the thermal critical points are given in the following tables showing the results of several hundred determinations. All the steels used in connection with the results given in Table II contained in the vicinity of one per cent carbon.

A magnetic method for the determination of the A_2 , $A_{3.2}$ or $A_{3.2.1}$ points has been described in Chapter X.

TABLE I. — COMPARISON OF THE MAGNETIC METHOD WITH THE ORDINARY OR COOLING-CURVE METHOD. (BOYLSTON.)

APPROXIMATE CARBON CONTENT OF STEEL	METHOD	Ac_{3-2-1}		NUMBER OF TESTS	Ar_{3-2-1}		NUMBER OF TESTS
		MEAN	MAX. MIN.		MEAN	MAX. MIN.	
1.25%	Magnetic	773	{ 788 759	7	708	{ 711 706	7
	Ordinary	764	{ 781 754	4	718	{ 736 701	4
0.40%	Magnetic	780	{ 790 770	7	741	{ 750 734	7
	Ordinary	827	{ 830 822	3	754	{ 756 753	3
0.15%	Magnetic	764	{ 772 755	6	764	{ 771 758	7
	Ordinary	768	{ 772 764	2	767	{ 783 748	3

TABLE II. — RESULTS OBTAINED BY STUDENTS AT HARVARD UNIVERSITY

STEEL NUMBER	METHOD	Ac_{3-2-1}	NUMBER OF TESTS	Ar_{3-2-1}	NUMBER OF TESTS
1	Magnetic	753	72	679	75
	Ordinary	739	14	688	12
2	Magnetic	752	131	695	136
	Ordinary	750	13	695	17
3	Magnetic	761	55	704	55
	Ordinary	757	55	708	55
4	Magnetic	762	50	700	50
	Ordinary	751	45	701	45
5	Magnetic	776	40	720	40
	Ordinary	760	30	727	30

Crystallization. — The cube being the crystalline form both of beta and of alpha iron and these two allotropic varieties being capable of dissolving each other in all proportions (Osmond) a crystalline transformation at the point A_2 is not to be expected. The crystallography of iron so far as it has been investigated does not reveal the existence of the point A_2 .

Tensile Strength. — Rosenhain and Humfrey have shown the existence of a distinct discontinuity in the tensile strength of iron at the A_2 point.

Dissolving Power for Carbon. — Most metallographists believe that alpha iron does not possess any dissolving power for carbon, or at least that it is only capable of dissolving a very small amount of that element. On the other hand, as already mentioned, it is far from certain that beta iron is incapable of dissolving carbon, statements to the contrary notwithstanding. It is possible, therefore, that on cooling through Ar_2 , iron loses its dissolving power for carbon.

Structural Properties. — By referring to Figure 179 of Chapter XI it will be seen that there is no apparent structural change connected with the point A_2 . As the steel cools past Ar_2 the liberation of ferrite started at Ar_3 merely continues, to end only at Ar_1 . Of course the ferrite liberated above Ar_2 now passes from the beta to the alpha condition, but this allotropic transformation does not appear to include any structural change.

Specific Heat. — Weiss and Beck and Meuthen have shown that a sharp discontinuity occurred in the specific heat of iron at the A_2 point.

CHANGES AT $A_{3.2}$

It has been shown that the point $A_{3.2}$ resulting from the merging of A_3 and A_2 occurs, theoretically at least, in steels containing from some 0.35 to 0.85 per cent carbon. As might be expected the changes of properties corresponding to the point $A_{3.2}$ are the same as those taking place in lower carbon steel at A_3 and A_2 . As the metal cools through $Ar_{3.2}$ the following variations of properties are, therefore, noted: (1) a marked dilatation, (2) a sudden decrease of electrical resistance, (3) a gain of magnetism, (4) a discontinuity in the variation of the tensile strength and of the specific heat, (5) a probable loss of dissolving power for carbon, (6) the beginning of the liberation of alpha ferrite (see Chapter XI, Fig. 180).

CHANGES AT A_1

The point A_1 occurs in steel containing from a mere trace to 0.85 per cent carbon. It corresponds, as explained in Chapter XI, to the transformation of the residual austenite (now of eutectoid composition) into pearlite. This formation of pearlite implies that the iron contained in this residual austenite (and forming about 85 per cent of its bulk) undergoes on cooling through Ar_1 the same allotropic changes as those affecting the free ferrite on cooling through Ar_3 and Ar_2 (or $Ar_{3.2}$). It follows from this that, theoretically at least, the following sudden changes of properties should be noted on cooling through Ar_1 : (1) a dilatation increasing with the carbon content and being maximum with 0.85 per cent carbon caused by the allotropic transformation of the iron, (2) increased magnetism because of the transformation of additional non-magnetic gamma iron into magnetic alpha iron, (3) decreased electrical resistance because of additional transformation of high resistance gamma iron into low resistance alpha iron, and (4) additional loss of dissolving power for carbon because of the formation of additional alpha iron.

The point A_1 is not generally associated with critical variations of the electrical and magnetic properties of steel, but on purely theoretical ground it does not seem possible to avoid the conclusion that such critical variations must exist provided of course that we are right in assuming that in austenite of eutectoid composition the

iron is still in the gamma condition, that is, non-magnetic and of high electrical resistance. Recent investigations have indeed shown that A_1 is distinctly a magnetic point.

CHANGES AT $A_{3.2.1}$

The point $A_{3.2.1}$ occurs in eutectoid and in hyper-eutectoid steel and marks the transformation of the austenite or eutectoid steel or of the residual austenite of hyper-eutectoid steel, into pearlite, as shown in Figures 181 and 182, Chapter XI. In these steels, however, no liberation of free ferrite occurs above the point $Ar_{3.2.1}$ from which it follows that the *totality* of the iron undergoes its allotropic change or changes on passing through $Ar_{3.2.1}$. The variations of the properties which in hypo-eutectoid steel occur at A_3 , A_2 , and A_1 must therefore, in the case of eutectoid and hyper-eutectoid steel all take place at the point $A_{3.2.1}$. These sudden changes of properties are, on cooling: (1) a marked dilatation, maximum in eutectoid steel (Fig. 186), (2) a sudden decrease of electrical resistance, (3) a sudden gain of magnetism, (4) a loss of dissolving power for carbon.

Le Chatelier mentions the fact that on cooling through Ar_1 or $Ar_{3.2.1}$ steel acquires a temporary malleability. If a steel bar, for instance, of sufficient length be held horizontally by one extremity while cooling, it at first remains rigid, but on passing through its point of recalescence it quite suddenly bends. According to Howe this phenomenon was first observed by Coffin.

Structural Change at A_1 and $A_{3.2.1}$. — The spontaneous transformation of austenite of eutectoid composition into pearlite, that is, of a solid solution into an aggregate, at Ar_1 or $Ar_{3.2.1}$ and the reverse transformation, from aggregate to solid solution, at Ac_1 , or $Ac_{3.2.1}$ imply structural changes of momentous importance to the steel metallurgist. While these will be dealt with at length in another chapter it seems proper to record here their significance. These structural changes give the key to the rational treatment of steel. They make possible the refining of steel by heat treatment seeing that on heating steel through its critical range we may change it from the condition of a coarse aggregate (a coarse structure) to the condition of a fine, nearly amorphous, solid solution. They also make possible the hardening of steel through sudden cooling from above the critical range as will be fully explained in another chapter.

CHANGES AT A_{cm}

The point Ar_{cm} occurs in hyper-eutectoid steel and marks the beginning of the liberation of free cementite as the metal cools from Ar_{cm} to $Ar_{3.2.1}$ (see Fig. 181, Chapter XI). Except for this structural change no other marked changes of properties have so far been connected with this point.

Prevailing Conditions Above and Below the Critical Range. — The following condensed statement of some of the most significant conditions prevailing above and below the critical range of iron-carbon alloys may be useful in keeping these fundamental facts in mind. By critical range is, of course, meant here the critical points, both on heating and cooling, considered collectively and it will be understood that the conditions described as existing above the range change quite abruptly to the conditions prevailing below the range as the metal cools through the range, or vice versa as it is heated above it. The references made to the crystallizing of the

metal, and to the influence of work both above and below the range will be understood after reading the following chapters dealing with the treatment of steel.

CONDITIONS AND PROPERTIES OF IRON-CARBON ALLOYS AND OF THEIR CONSTITUENTS

Above Critical Range

Solid solution (austenite).
Hardening (dissolved) carbon.
Gamma iron.
Alloys containing a sufficient amount of carbon possess hardening power.
Alloys are non-magnetic.
Metal crystallizes on slow cooling.
Work prevents crystallization.

Below Critical Range

Aggregate (ferrite + cementite).
Cement carbon (Fe_3C).
Alpha iron.
Same alloys deprived of hardening power.
Alloys are magnetic.
Metal does not crystallize on slow cooling.
Work distorts structure.

Properties of Gamma, Beta, and Alpha Iron. — The various properties of gamma, beta, and alpha iron described in the preceding pages, have been tabulated below as well as some other data of interest. These are in accordance with the views held by many, but the author is well aware that those entertaining different views may take exception to some of the entries.

	GAMMA IRON	BETA IRON	ALPHA IRON
Metallurgical name	Austenite	Beta ferrite	Ferrite, alpha ferrite, pearlite ferrite
Solvent power for C (or Fe_3C)	dissolves carbon up to 1.7 per cent or Fe_3C up to 25.5 per cent	probably some but opinions differ	probably none, but opinions differ
Range of temperature in which stable	above A_3 , $A_{3.2}$, or $A_{3.2.1}$ in case of pro-eutectoid ferrite, above A_1 or $A_{3.2.1}$ in case of eutectoid ferrite	as free beta ferrite between A_3 and A_2	below A_3 , $A_{3.2}$, or $A_{3.2.1}$
System of crystallization	cubic (orthorhombic according to Le Chatelier)	cubic	cubic
Prevailing crystalline forms	octahedra	cubes	cubes
Other crystalline characteristics	frequent twinings	no twinings	no twinings
Specific gravity	greater than beta and alpha iron (dilatation at A_3)	greater than alpha iron (gradual dilatation at A_3 , Osmond)	smaller than gamma and beta iron
Electric conductivity	ten times smaller than that of alpha iron at ordinary temperature	greater than that of gamma iron and increasing with falling temperature	greater than that of beta iron and increasing with falling temperature
Magnetic properties	non-magnetic	feebly magnetic	strongly magnetic
Hardness	softer than beta iron, harder than alpha iron	very hard	soft

CHAPTER XIII

CAST STEEL

The structural and other changes taking place at the thermal critical points of steel account for the deep changes of properties resulting from the treatments to which steel is subjected in the process of manufacture of steel objects. We are now in a position to understand these changes, to anticipate them, and to arrive at the rationale of the treatment of steel which for so many centuries remained purely empirical.

It is logical that we should first consider the structure of steel before it has received any treatment whatsoever, namely, the structure of the metal in its cast condition. To this study the present chapter will be devoted.

The structure of cast steel is different from what, in these chapters, has been termed the normal structure of the metal because, having been developed during very slow and undisturbed cooling from the molten condition, crystalline growth has been promoted, whereas in working and reheating such large growth is hindered or corrected. It may well be expected then that the structure of steel castings will be coarser, as is generally expressed, that is, made up of larger crystalline grains, than the normal structure so far considered, and therefore that steel castings will suffer from all the ills that pertain to a coarse structure, namely, weakness, lack of ductility, or even brittleness, etc. It will be profitable to consider first the crystallization of steel in general and then the genesis of the structure of cast eutectoid, hypo-eutectoid, and hyper-eutectoid steel.

Crystallization of Steel. — We are indebted to Colonel Belaiew more than to any one else for our knowledge of the crystallization of steel. His views will be briefly described.

The crystallization taking place during the solidification period is called by Belaiew "primary crystallization"; it consists in the formation of dendrites of a solid solution of iron and carbon (austenite), all steels immediately after solidification being built up of juxtaposed and interlocked dendrites mutually limiting each other. If during the process of solidification the molten mother-metal is withdrawn "isolated crystals" are exposed to view (see Chapter V, Fig. 123). The dendrites of the primary crystallization are composed of octahedra, the octahedron being the crystallographic form of iron and steel. According to Belaiew this primary crystallization may be detected on the surface of steel samples under favorable conditions while it may be brought out on polished surfaces by a prolonged etching with dilute acids as recommended by N. J. Belaiew. The structure is then frequently "macroscopic," that is visible with the naked eye. A remarkable instance of this primary dendritic structure in manganese steel is shown in Figure 190.

Stead depicts this primary crystallization in Figure 191 which represents the gradual growth of three separate crystals. The dark crystallites in A feed and de-

velop out of liquid, abstracting the iron and concentrating the carbon in portions that still remain liquid. The white junctions in C and D represent the last portions of liquid metal, rich in carbon, also sulphur and phosphorus, if any happens to be present. Stead writes: "the fine fir-tree crystallites, containing probably a fraction of the amount of the carbon in the liquid steel, grow steadily forward from the cold surfaces of the containing moulds. The crystallites develop branches in three direc-



Fig. 190. — Manganese steel magnified 62 diameters.

tions corresponding to the axes of the cube, and these branches throw out similar branches themselves. Eventually parts of the most fusible portions are trapped between the branches and are the last to solidify. When there is much phosphorus or some sulphur in the metal, they are always present together with an excess of the carbon in the last residue of metal that remains liquid and although in cooling down, after the liquid has solidified, the excess carbon diffuses out of it into the purer part,

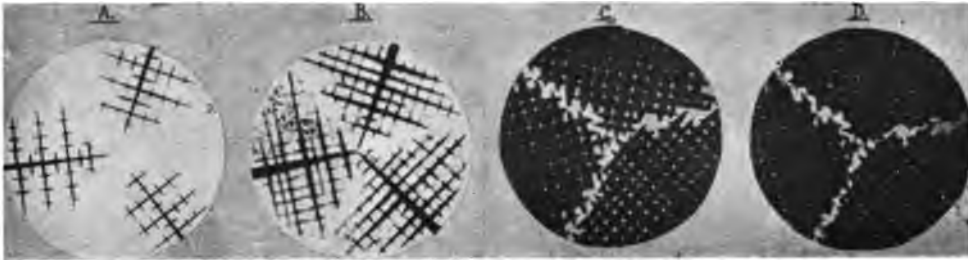


Fig. 191. — Diagram representing the gradual growth of three separate crystals. (Stead.)

the sulphides and phosphides do not, but remain fixed, and can generally be detected in the solid metal."

Immediately after the solidification is completed a crystalline transformation starts in, which Belaiew calls "granulation." This granulation continues until the critical range of the metal is reached, all steels being then made up of a number of grains, each grain built up of small octahedra and having its own orientation. This granulated structure generally called austenitic or polyhedral (Guillet) may be re-

vealed by etching the steel while still in its granulating zone, that is above its critical range, with hydrochloric acid (Osmond's method). It will be shown elsewhere that in the case of some alloy steels, notably with certain manganese and nickel steels, this granulated structure is preserved at atmospheric temperature when it can be

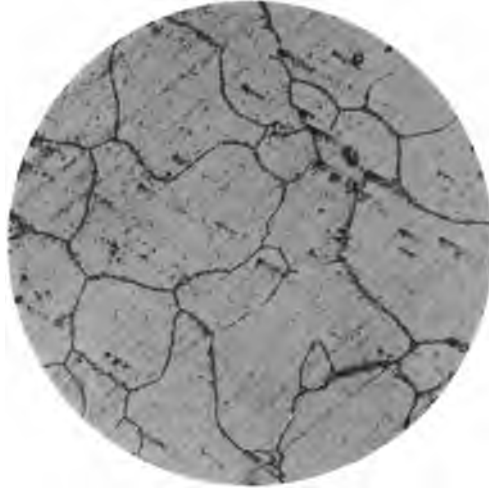


Fig. 192. — Manganese steel. Cast. Heated to 1000 deg. C. and quenched in water. Reheated for two hours at 700 deg. C. and furnace cooled. Magnified 100 diameters.

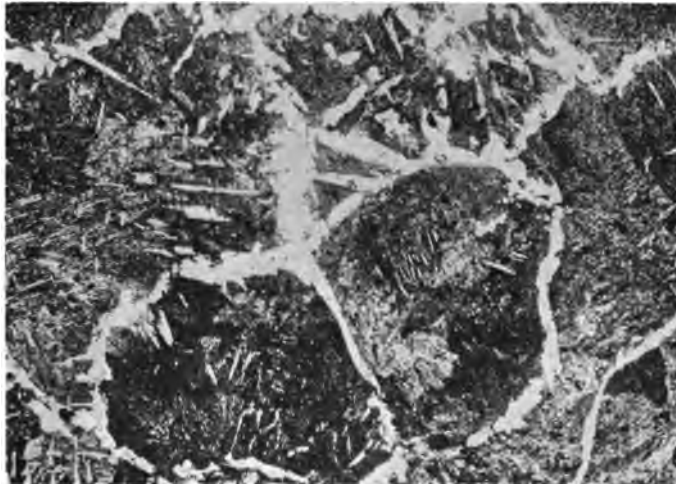


Fig. 193. — Steel containing about 0.50 per cent carbon. Cast. Magnified 100 diameters. (R. W. Smyth in the author's laboratory.)

revealed by the ordinary etching methods (Fig. 192). Generally speaking the longer the sojourn in the granulation zone and the slower the cooling the larger will be the austenite grains on reaching the critical range and, as later explained, the coarser the final structure of the steel after slow cooling through the range.

In passing through the critical range as previously described the excess ferrite of hypo-eutectoid steel or the excess cementite of hyper-eutectoid steel is rejected by each austenite grain until finally in cooling through Ar_1 the remaining portions of

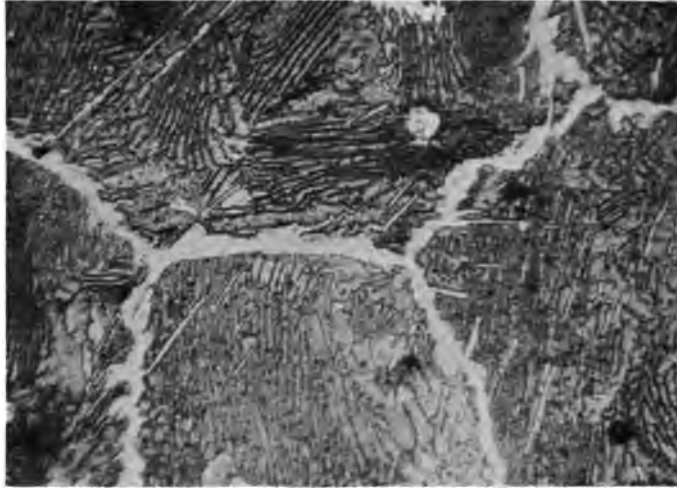


Fig. 194. — Steel. Hyper-eutectoid. Magnified 100 diameters.
(R. W. Smyth in the author's laboratory.)



Fig. 195. — Hypo-eutectoid steel. Cast. Free ferrite rejected chiefly between cleavage planes. Magnified 100 diameters. (W. J. Burger, Correspondence Course student.)

each grain, now necessarily of eutectoid composition, are converted bodily into pearlite. This important crystalline transformation taking place as the steel cools through its critical range is called by Belaiew "secondary crystallization." The resulting

structures which are retained after complete cooling are readily revealed by the ordinary etching methods. Very slow cooling while this secondary crystallization is taking place promotes the rejection of the excess constituent (ferrite or cementite) to the boundaries of the grains giving rise after complete cooling to so-called network or cellular structures which are so frequent in steel forgings, and in which each grain of pearlite is surrounded by a membrane of ferrite in hypo-eutectoid steel and of cementite in hyper-eutectoid steel (Figs. 193 and 194). If during the secondary crystallization, however, the cooling is quite rapid, the excess constituent is for



Fig. 196. — Steel. Carbon 0.55 per cent. Widmanstätten structure. Magnified 6 diameters. (Belaiew.)

the most part retained between the cleavage planes of the small octahedra composing each grain, probably because the necessary time is denied for this excess constituent to reach the boundaries of the grains. This type of structure is of frequent occurrence in steel castings (Fig. 195) and is intensified by a long sojourn in the granulation range of temperature because such treatment results in the formation of larger grains. This structure which might be described as “cleavage” structure is frequently called “Widmanstätten” structure in memory of A. Widmanstätten who in 1808 discovered its existence in certain meteorites. To sum up, the network or

cellular type of structure is developed in steel castings by slow cooling through the critical range, especially through the upper part of the range (i.e. through Ar_3 , Ar_2 , $Ar_{3.2}$, or Ar_{cm} , as the case may be, down to Ar_1) when the excess constituent separates from the solid solution. The longer the exposure of the metal in the granulation range, that is between the end of the solidification and the beginning of the critical range, the larger generally the meshes or cells and, therefore, also the pearlite grains. Very slow cooling through the granulation range also promotes the formation of large grains first of austenite and later of pearlite. The cleavage or Widmanstätten type of structure is promoted by long sojourn in the granulation range and slow cooling in that range and by relatively quick cooling through the critical range, especially

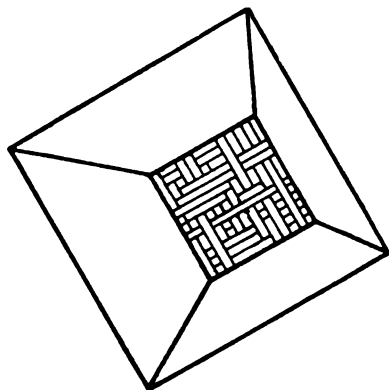


Fig. 197. — Section parallel to the surface of a cube. (Tschermak.)



Fig. 198. — Steel. Carbon 0.55 per cent. Section parallel to the surface of a cube. Magnified 30 diameters. (Belaiew.)

through the upper part of the range while the excess constituent is being rejected. The Widmanstätten structure is, generally speaking, more brittle than the network type.

Belaiew succeeded in a remarkable manner in reproducing the Widmanstätten structure by subjecting carbon steels to suitable treatments. The structures obtained by him in the case of steel containing 0.55 per cent carbon and otherwise of commercial quality are shown in Figures 196 to 203. They are typical structures of steel castings of the same grade but on a much larger scale, for it should be noted that the magnification of Figures 198 to 203 is only 30 diameters while Figure 196 is magnified but 6 diameters. Figure 196 is a beautiful illustration of that type of structure in which the free ferrite has been rejected both to the grain boundaries forming a sharply outlined network and between crystallographic planes. In Figures 198 to 203 the free ferrite is seen massed between cleavage planes.

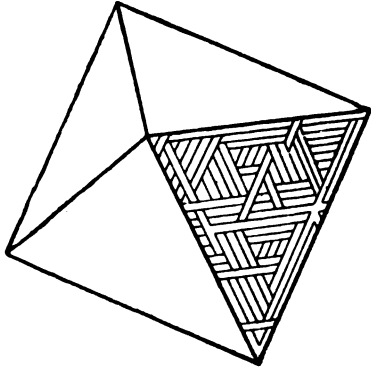


Fig. 199. — Section parallel to the surface of an octahedron. (Tschermak.)



Fig. 200. — Steel. Carbon 0.55 per cent. Section parallel to the surface of an octahedron. Magnified 30 diameters. (Belaiew.)

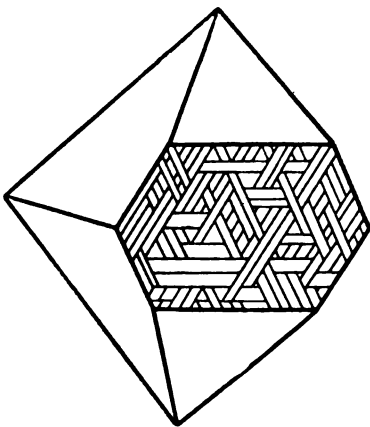


Fig. 201. — Section parallel to the surface of a dodecahedron. Magnified 30 diameters. (Tschermak.)



Fig. 202. — Steel. Carbon 0.55 per cent. Section parallel to the surface of a dodecahedron. Magnified 30 diameters. (Belaiew.)

Octahedric Crystallization of Austenite. — It will be noted that the ferrite bands shown in Figures 198 to 203 cut each other at right angles or, more frequently, form equilateral triangles. According to crystallographers these are indications that austenite crystallizes in regular octahedra. That this inference is correct appears to be conclusively proven by the following remarks of Belaiew:

“Let us consider an octahedron and let us assume that four systems of lamellæ locate themselves in this octahedron along its crystallographic planes, that is, parallel to the four pairs of its surfaces, a fact that has been long known in the case of meteoric irons.

“If we now examine any section of the octahedron, we shall find that not only the angles formed by the projections of the lamellæ vary in different sections, but that the number itself of different sections varies likewise from two to four. For instance, when the section is parallel to the surface of the cube, the number of different sections is minimum, that is, two, and in the entire section we



Fig. 203. — Steel. Carbon 0.55 per cent. Four systems of lamellæ. Magnified 30 diameters. (Belaiew.)

find only two systems of lamellæ forming right angles. Figure 197 is a diagram of such section and Figure 198 a corresponding section of the steel.

“A section parallel to one of the surfaces of the octahedron will yield equilateral triangles formed by three systems of lamellæ forming 60° angles; the fourth system coincides with the section considered (see Figs. 199 and 200).

“In a section parallel to the surface of the dodecahedron, two systems of lamellæ are observed forming an angle of $109^\circ 28' 16''$; the other two systems coincide and divide this angle in half (Figs. 201 and 202). Finally any section will give four different systems cutting each other at different angles (Fig. 203).

“All these cases, as we have just seen, can very well be illustrated by different samples of our alloy which, firstly, affords a rather weighty proof of the octahedric crystallization of steel and, secondly, brings out the remarkable analogy of this structure with that of meteorites and warrants us to allude to the synthesis of the structure so called of Widmanstätten . . . this structure is the necessary consequence of the uniform orientation of the elementary octahedra within a volume of greater or less dimension; it is, therefore, in no way related with the carbon content and must be obtained

in any alloy of iron and carbon whenever the conditions are favorable to the formation of that structure.

"Moreover, in practice this structure is met (although certainly much less developed than in our alloys) every time that the metal is subjected to an intense heating followed by slow cooling as is the case with cast steel or, better still, with burnt or overheated steel.

"The very brittleness of these steels may be due to a certain extent to the uniform orientation of the elementary octahedra which are the cause of that structure."

Let it be noted that in the case of meteorites the length of time during which the metal is maintained at a high temperature is so long that generally but one crystal is formed, that is, all the elementary octahedra formed on solidification have assumed the same orientation. In steel the conditions being less favorable to uniformity of orientation we have several grains.

Structure of Cast Eutectoid Steel. — Above its melting-point eutectoid steel consists, like all steels, of a liquid solution of carbon or of the carbide Fe_3C in iron. It solidifies as a solid solution (austenite) of the same constituents, dendritic crystals



Fig. 204. — Eutectoid steel. Cast. Magnified 500 diameters. (Boylston.)



Fig. 205. — Hypo-eutectoid steel. Cast. Free ferrite rejected chiefly to the boundaries. Magnified 100 diameters. (H. C. Cridland in the author's laboratory.)

made up of small octahedra being formed. After solidification granulation takes place and remains active down to the beginning of the critical range which in eutectoid steel is reduced to the single point $\text{Ar}_{3.2.1}$, the metal being now made up of crystal-line grains of austenite. In passing through this point the austenite grains are converted bodily into as many pearlite grains, as explained in Chapter XI, a coarse austenitic structure acquired at a high temperature giving rise to a coarse pearlitic structure at ordinary temperature. The polyhedral structure, therefore (Fig. 204), observed after complete cooling indicates the original polyhedral structure of austenite formed above the critical point. Because of a coarser grain and coarser pearlite cast eutectoid steel is weaker and less ductile than eutectoid steel properly worked or annealed or both.

Structure of Cast Hypo-Eutectoid Steel. — Let us now consider the genesis of the structure of hypo-eutectoid steel, and let us select as an example steel containing

0.60 per cent carbon and, therefore, composed after complete slow cooling of 72 per cent of pearlite and 28 per cent of free ferrite. The formation of the structure of this steel has been depicted in Figure 180, Chapter XI, to which the reader is referred. This steel on solidifying passes, like all steels, from the condition of a liquid solution of iron and carbon to that of a solid solution of carbon (or more probably Fe_3C) in gamma iron, first dendrites and then, through granulation, crystalline grains of austenite being formed. These grains continue to grow as the steel cools slowly to its upper critical point $\text{Ar}_{3.2}$ when, as explained in Chapter XI, ferrite begins to be liberated and continues to be liberated as the metal cools to its lower point Ar_1 . This setting free of ferrite is apparently brought about by each grain of austenite rejecting the ferrite in excess of the eutectoid composition, so that by the time the point Ar_1 is reached each residual grain of austenite has the eutectoid composition and on cooling through Ar_1 is converted bodily into a grain of pearlite. Microscopical examination reveals the fact that the pro-eutectoid ferrite is rejected (1) to the boundaries of the decreasing austenitic grains and (2) between the cleavage or crystallographic planes of these crystalline grains, so that three types of structures may be distinguished in cast hypo-eutectoid steel, (a) structures in which the free (pro-eutectoid) ferrite has been rejected chiefly to the boundaries of the austenitic grains (Fig. 205), clearly indicating that these grains were polyhedral, (b) structures in which the free ferrite has been rejected chiefly between the cleavage planes of austenite (Fig. 195), proving the crystalline character of that constituent and suggesting that its crystallization is cubic, and (c) structures in which the free ferrite has been rejected partly to the grain boundaries and partly between the cleavage planes. Long exposure to high temperatures followed by rapid cooling through the critical range appears to favor the massing of free ferrite between crystallographic planes, whereas short exposure and slower cooling promotes the expulsion of free ferrite to the grain boundaries, resulting in sharply defined network structures.

The structure of cast hypo-eutectoid steel is coarse (1) because its slow and undisturbed cooling promotes the formation of large austenite grains and hence, later, of large pearlite grains, (2) because its slow cooling between the upper and lower critical points favors the rejection of a maximum amount of free ferrite which rejection makes for coarseness of structure, and (3) because its slow cooling from the upper critical point to atmospheric temperature promotes the crystallization of free ferrite into large grains, this influence, however, being material only where there is a large amount of free ferrite, i.e. in very low carbon steel.

Because of its coarser structure cast hypo-eutectoid steel is less tenacious and less ductile than forged or properly annealed steel of similar composition.

Structure of Cast Eutectoid vs. Structure of Cast Hypo-Eutectoid Steel. — Although the pearlite grains of eutectoid steel may be and often are larger than the pearlite grains of hypo-eutectoid steel, the latter, especially when judged by its fracture, is the coarser of the two. This greater coarseness of hypo-eutectoid steel in spite of smaller pearlite grains is due to the presence of free ferrite, relatively small pearlite grains surrounded by coarse ferrite envelopes or holding coarse ferrite particles imparting a coarse appearance to the fracture of steel. The dimension of the pearlite grains, therefore, while not without influence, is not the criterion by which to judge of the coarseness or fineness of the structure and fracture of hypo-eutectoid steel, the amount of free ferrite present and its mode of distribution having to be taken into consideration. In very low carbon steel, moreover, there is but little

pearlite and the small amount present occurs as small irregular particles exerting but little influence upon the character of the fracture which now depends quite exclusively upon the dimension of the ferrite grains. As ferrite grains, however, no matter how small never impart as fine a structure or fracture to steel as pearlite grains, it follows that low carbon (ferritic?) steels can never have as fine a structure or fracture as higher carbon (pearlitic) steels.

Structure of Cast Hyper-Eutectoid Steel. — The genesis of the structure of cast hyper-eutectoid steel has been depicted diagrammatically in Figure 181, Chapter XI. Between its solidification point and its upper critical point (A_{cm}) this steel is composed, like all steels, of crystalline austenite grains. Upon reaching the point A_{cm} the setting free of cementite begins, ending only at the lower point $A_{s,2.1}$. This free

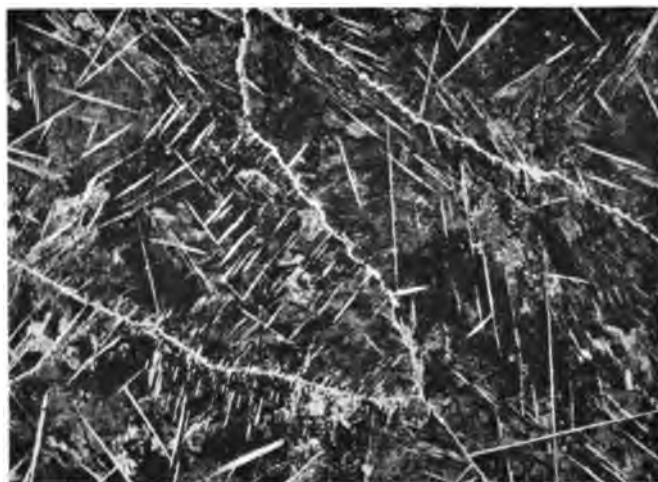


Fig. 206. — Hyper-eutectoid steel. Cast. Free cementite rejected partly to the boundaries and partly between cleavage planes. Magnified 114 diameters. (Boylston.)

cementite, like the free ferrite of hypo-eutectoid steel, is rejected (1) to the boundaries of the diminishing austenite grains and (2) between the cleavage planes of this crystalline austenite, giving rise to the three types of structure described in the case of hypo-eutectoid steel, but in which free ferrite is replaced by free cementite, namely, (a) structures in which the free cementite is found chiefly at the grain boundaries, (b) structures in which the free cementite is chiefly located between cleavage planes, and (c) structures in which the free cementite is partly at the boundaries and partly between crystallographic planes (Fig. 206). Like the structure of cast hypo-eutectoid steel, the structure of cast hyper-eutectoid steel bears witness (1) to the polyhedral form of the austenite grains, (2) to the crystalline character of these grains, and (3) to their probable cubic crystallization.

Long exposure to high temperatures followed by relatively rapid cooling between A_{cm} and $A_{s,2.1}$ promotes in hyper-eutectoid steel the rejection of cementite to the cleavage planes, while short exposure and slower cooling favor the rejection of cementite to the boundaries.

The rejection of free cementite, like the rejection of free ferrite, makes for coarseness of structure and fracture, from which it follows that cast and slowly cooled hyper-eutectoid steel will be coarser than cast and slowly cooled eutectoid steel, and that the more free cementite it contains, that is, the higher the carbon, the coarser it will be. The structure and fracture of hyper-eutectoid steel, however, will generally be decidedly finer than that of hypo-eutectoid steel because of the very small amount of free cementite present in the former compared to the amount of free ferrite in the latter, unless, indeed, the hypo-eutectoid steel be very near the eutectoid composition. This is due to the fact, now well understood, that starting from the eutectoid composition (carbon 0.85 per cent), as the carbon decreases the amount of free ferrite increases rapidly, while as the carbon increases above the eutectoid ratio the amount

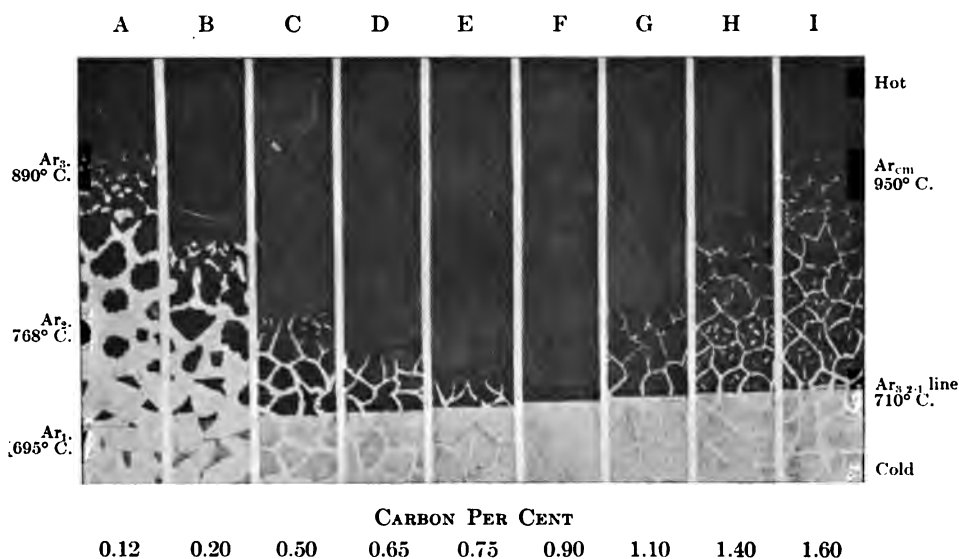


Fig. 207. — (Stead.)

of free cementite increases slowly and remains small even with high carbon content. Steel with 0.50 per cent carbon, for instance, contains 40 per cent of free ferrite, hence its coarseness both of structure and fracture, while steel with say 1.25 per cent carbon contains but 6.4 per cent of coarsening free cementite, hence the relative fineness of both its structure and fracture.

The rejection of the "excess" constituent (ferrite or cementite) and the formation of the final pearlitic structure in steels of varying carbon contents has been interestingly depicted by Stead (Fig. 207). A, B, C, D, and E are hypo-eutectoid steels containing increasing percentages of carbon, F is steel of eutectoid composition, G, H, and I hyper-eutectoid steels of increasing carbon contents. The diagram clearly shows (1) that in hypo-eutectoid steel, as the carbon increases, the rejection of the free ferrite (the white constituent) by the solid solution (the black portion) begins at progressively lower temperatures (the A_{r_3} or $A_{r_{3.2}}$ point) and that the amount rejected decreases steadily, (2) that in hyper-eutectoid steels, with increasing carbon, cementite is rejected in larger proportions and at increasing temperatures (the $A_{r_{cm}}$

point), (3) that at the Ar_1 or $Ar_{3.2.1}$ point the remaining solid solution (black portion) is converted bodily into pearlite (the shaded portion), (4) that a coarse austenitic structure developed above the Ar_1 point implies the formation of a coarse pearlitic structure below that point, and (5) that with some 0.50 or more per cent carbon the excess constituent frequently forms membranes surrounding pearlite grains and giving rise to so-called network, cellular, or polyhedral structures.

Ingotism. — Howe has suggested the term “ingotism” to designate the structure of cast steel described in the foregoing pages and characterized (1) by large pearlite grains and (2) by coarse ferrite or cementite membranes surrounding them and by irregular masses of these constituents located in some of the cleavage planes of the original austenite grains.

CHAPTER XIV

THE MECHANICAL TREATMENT OF STEEL

Forged steel objects are manufactured by subjecting the cast metal (1) to pressure exerted by rolls, presses, or dies, or to blows from hammers and (2) by reheating it to various temperatures for various lengths of time and cooling it at various rates. In other words we have to consider (1) the mechanical treatment of steel and (2) its heat or thermal treatment. The machining of steel is not here mentioned since it can evidently have no effect upon the structure and properties of the metal, unless it be a very superficial one.

While the primary purpose of working steel is to shape it into useful appliances and while the primary purpose of reheating it may be, and often is, to impart to the metal such plasticity as will facilitate its being so shaped, both mechanical and heat treatments deeply affect the structure of steel and therefore its physical properties. To this very important subject the next four chapters will be devoted. We shall first consider the influence of mechanical treatment and then that of heat treatment.

The effect of work upon the structure and properties of steel greatly depends upon the temperature of the metal while it is being worked, the expressions "hot working" and "cold working" being common ones, the former meaning working the steel while hot, and the second working it while cold, more specifically at atmospheric temperature. In these pages the expression hot working will be applied to working the metal while above its critical range, and cold working to work performed below that range. In justification of this course it will be shown that the effect of work changes quite sharply as the critical temperature of steel is passed.

Hot Working. — Hot working may be applied to steel (1) after it has solidified but before it has cooled to a much lower temperature so that it still possesses the necessary plasticity, or (2) the steel ingot may be allowed to cool to atmospheric temperature or at least to a temperature so low that reheating is required as a preliminary step to successful hot working. The following considerations will show that so far as the influence of hot work is concerned it is quite immaterial whether the steel ingot has or has not been completely cooled before being brought to the forging temperature. Let us assume that the steel ingot be allowed to cool to atmospheric temperature, that it is then reheated to a temperature well above its critical range and then subjected to hot working.

An attempt has been made in Figure 208 to depict graphically the influence of hot work on the structure of steel. The diagram will be readily understood. The critical range both on heating and cooling is represented by a double line, but the reader will, of course, bear in mind that the critical range on heating does not coincide with the range on cooling and that each range may include one, two, or three critical points, as fully explained in previous chapters. For the present purpose it is preferable

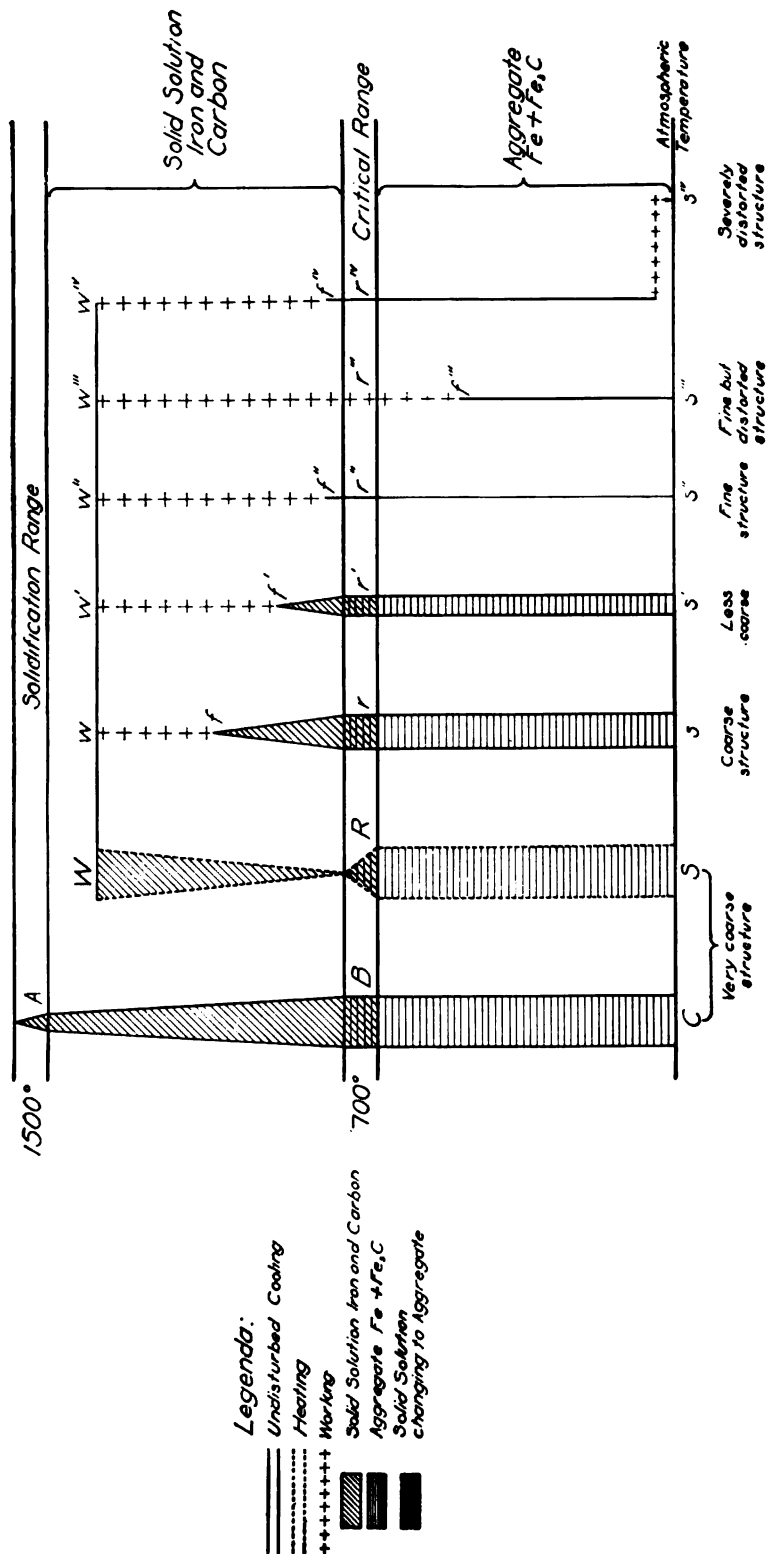


Fig. 208. — Diagram depicting the influence of work upon the structure of steel.

to represent both ranges irrespective of the number of critical points included by the two parallel lines shown in the diagram. The solidification range is likewise indicated by a double line. The widths of the shaded areas are intended to be proportional to the grain size resulting from the various treatments; when an area is reduced to a mere line the corresponding grain is very small, i.e. the structure very fine. As the steel ingot solidifies at *A* crystalline grains are formed which increase in size on slow and undisturbed cooling to the critical range *B*. In passing through that range the austenite grains are converted into pearlitic grains with or without rejection of free ferrite or of free cementite according to the carbon content of the steel. On cooling from *B* to *C* there is no further growth and the size of the final grain may be represented by the width of the shaded area at *C*. The metal has now the usual coarse structure of steel castings described in Chapter XIII. Upon reheating this coarsely crystalline steel ingot from *S* to *R* and through its critical range, it is converted from the condition of an aggregate of ferrite and cementite into a nearly amorphous solid solution, so that as the metal emerges from its range it has a very fine structure. As steel just above its critical range, however, would not be plastic enough for hot working and would not afford the necessary range of temperature through which to cool while being worked and still remain, as it should, above the range, it is generally necessary to heat the metal to a much higher temperature, say to some 1200 deg. C. or even more (*W* in Fig. 208). As the metal is heated from its critical range to this high temperature, it probably crystallizes so that when work begins at *w* it is in a somewhat crystalline condition. This grain growth on heating from *R* to *W* is depicted in the diagram. The heavy pressure or blows which are now applied, however, soon break up this crystallization while preventing a new one from forming, so long at least as the work continues sufficiently vigorous, for *undisturbed* cooling is a condition necessary for the ready growth of crystals. As soon as work ceases, however, the metal being now left to cool undisturbedly, if its temperature is then above its critical range, for instance at *f*, it will immediately begin to crystallize and its crystallization will continue from *f* to *r*, that is until its critical range is reached, when it will stop and the austenite grains just formed will be converted into as many pearlite grains with or without rejection of free ferrite or free cementite. The width of the band at *s* is intended to represent the size of the final grain. It is smaller than the grain of the steel ingot but it is still large.

If work ceases, then, while the metal is still above its critical range it is evident that it will crystallize and that the resulting grains will be the larger, that is its structure will be the coarser, the higher the temperature at which the work was stopped.

Finishing Temperatures. — The temperatures at which work ceases are known as the finishing temperatures and the above considerations will show the importance of proper finishing temperatures if it be desired to impart to steel implements the finest grain that it can acquire through working together with the desirable properties inherent to it.

Should hot work be continued, for instance, until the temperature of the metal is but slightly above its critical range, *f'* in Figure 208, the austenitic grains that will form on undisturbed cooling to the range will be small, so that the final grain of the metal at *s'* will likewise be small, as indicated by the width of the shaded area. If the finishing temperature is exactly at the critical range, *f''*, the final grain at *s''* will be very fine. If working be continued until the metal has cooled to a temperature

lower than its critical range, for instance f''' in the diagram, the structure will be fine since crystallization was prevented while the metal was cooling above its critical range, but it will be distorted because the effect of working below the range, that is of cold working, is to distort the structure as explained in the following pages. A distorted structure in turn means decreased ductility and eventually brittleness. It seems evident, therefore, that hot worked steel implements should be finished exactly at their critical ranges or at temperatures but slightly superior or inferior to them.

Structure of Hot-Worked Eutectoid Steel. — If eutectoid steel be subjected to hot work until it has nearly reached its critical range (now consisting of the single point $Ar_{3.2.1}$), f'' in Figure 208, it will have a very fine austenitic structure which in cooling slowly and undisturbedly through the critical range at r'' will be converted



Fig. 209. — Steel. Eutectoid. Hot-worked. Magnified 100 diameters. (Boylston.)



Fig. 210. — Hot-worked hypo-eutectoid steel. Carbon 0.50 per cent. Finishing temperature near critical range. Magnified 100 diameters. (Burger, Correspondence Course student.)

into a fine pearlitic structure. The metal will then have as fine a structure as can be imparted to it by work alone, followed by slow cooling through the range.

If eutectoid steel be worked until its temperature is still considerably above its critical point (f , Fig. 208), and then allowed to cool undisturbedly, austenite grains begin to form and increase in size as the metal cools to its critical point, i.e. from f to r when these austenitic grains are converted into as many pearlitic grains. The final grain size therefore will depend upon the temperature at which work ceased and will be the greater the higher that temperature.

The structure of hot worked eutectoid steel is shown in Figure 209 under a magnification of 100 diameters.

Structure of Hot-Worked Hypo-Eutectoid Steel. — If hypo-eutectoid steel be worked until its temperature is but slightly above its critical range (f'' , Fig. 208) and then allowed to cool undisturbedly, small grains of austenite are formed which on passing through the critical range at r'' are converted into pearlite grains with rejection of excess ferrite as now well understood (Fig. 210). When finished at

higher temperatures, "network" structures are often produced (Fig. 211) the bulk of the free ferrite forming membranes surrounding grains of pearlite (or of sorbite). Generally speaking the meshes of the network will be the larger, the higher the finishing temperature.¹

In the case of low carbon steel, however, containing say less than 0.30 per cent carbon the proportion of free ferrite is so large, i.e. the ferrite net so thick, that the structure consists of particles of pearlite embedded in a matrix of ferrite (see Fig. 212 and also Fig. 207, A and B).

Structure of Hot-Worked Hyper-Eutectoid Steel. — If hyper-eutectoid steel be hot worked until its temperature is very near its critical range (f'' , Fig. 208) and then allowed to cool undisturbedly, small austenite grains are formed which on cooling through the range are converted into small pearlite grains with rejection of

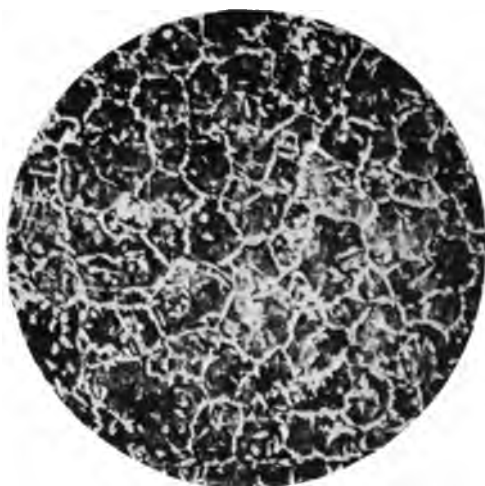


Fig. 211. — Hot-worked hypo-eutectoid steel. Carbon 0.50 per cent. Finishing temperature considerably above the critical range. Magnified 56 diameters.

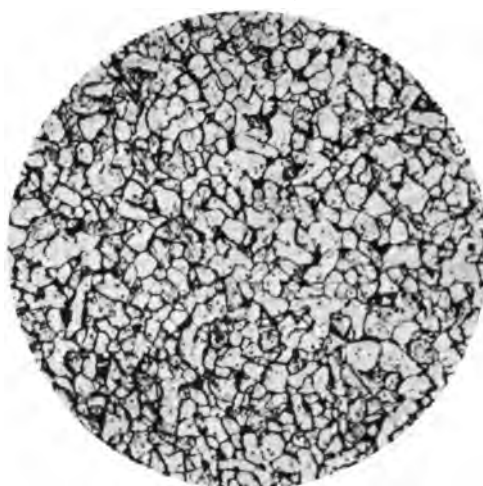


Fig. 212. — Hot-worked hypo-eutectoid steel. Carbon 0.05 per cent. Magnified 114 diameters. (Boylston.)

free cementite, as shown in Figure 213. If the work be stopped at a temperature considerably above the critical range (f , Fig. 208), the final pearlite grains will be larger while the free cementite will be located chiefly at the grain boundaries, a network structure being produced. It will be evident that a close relation exists between the size of the meshes of these network structures and the corresponding finishing temperatures.

Sorbite. — High magnification of the structure of the meshes of both hypo- and hyper-eutectoid steel described in the foregoing pages often fails to reveal the characteristic features of pearlite, namely, (1) sharply defined parallel plates alternately

¹ The accuracy of this statement has been questioned by some recent writers, notably by W. R. Shimer, who studying the microstructure of steel rails finished at different temperatures concludes that the structure is affected more by the rate of cooling than by the finishing temperature. The author's investigations, on the contrary, have always pointed consistently to the marked influence of finishing temperature on grain-size.

of ferrite and cementite and (2) a constant or nearly constant carbon content. The structure of these meshes instead remains indistinct and presents a granular rather than a lamellar aspect (Fig. 214). It is also frequently noted in connection with these network structures that the full amount of free ferrite or of free cementite has not been rejected, the pearlitic grains having retained some of the constituent in excess of the eutectoid ratio. To this imperfectly developed pearlite the name of sorbite has been given (Osmond) and quite universally adopted in spite of recent and regrettable efforts to eliminate it from metallographic nomenclature. It will be apparent that the formation of sorbite results from a relatively quick cooling through the critical range, time being denied for the crystallization of distinct lamellæ of ferrite and



Fig. 213. — Hot-worked hyper-eutectoid steel. Carbon 1.50 per cent. Finishing temperature near critical range. Magnified 100 diameters. (Reinhardt in the author's laboratory.)

cementite and, in the cases of hypo- and hyper-eutectoid steel, for the rejection of the full amount of free ferrite or free cementite. The cooling in air of hot-worked pieces, especially when of small size, is often sufficiently rapid to cause the formation of sorbite rather than of pearlite.

The production and nature of sorbite will be dealt with at greater length in another chapter. It should be mentioned here, however, that while sorbite is less ductile than pearlite it has a higher tenacity, higher elastic limit, and greater hardness (hence greater wearing power). When these qualities are required, in hot-forged objects, they may consequently be obtained, although necessarily at the sacrifice of some ductility and softness, by hastening the cooling through the critical range, after work has ceased, when sorbitic rather than pearlitic steel will be produced.

Hot Working of Steel vs. Its Critical Range. — In conducting the hot working of steel so as to impart to the metal the finest grain that can result from finishing at suitable temperatures, it is generally necessary only to consider its lower critical

point on cooling, namely, Ar_1 or $Ar_{3.2.1}$. The following considerations will justify this statement. In the case of hypo-eutectoid steel if the working be continued while the metal cools from its upper point or points to its lower point, it will make for fineness of structure by preventing a coarse massing of the free ferrite while the cold working of that constituent, if taking place at all, must be very slight. The same reasoning applies, with greater force, to the hot working of hyper-eutectoid steel from its upper point (denoting the formation of free cementite) to its lower point $Ar_{3.2.1}$. Greater fineness of structure will result with very little, if any, distortion of the free cementite.

It is apparent, therefore, that in order to secure the finest grain obtainable through mechanical refining without appreciable structural distortion steel objects should be



Fig. 214. — Hot-worked steel. Carbon 0.50 per cent. Magnified 650 diameters.

finished slightly above their lower critical point, that is, in the vicinity of 700 deg. C. for all grades of commercial carbon steel.

Cold Working. — By the cold working of steel is meant in these pages the working of it while its temperature is below its critical range. It will now be shown that the effect of cold working upon the properties of the metal is very different from that of hot working. This should not be a cause for surprise if it be borne in mind that steel above its critical range is in a condition totally different from its condition below it. Above the critical range we have to deal with a solid solution of iron and carbon, below it with an aggregate of ferrite and cementite. The solid solution existing above the range will crystallize if allowed to cool undisturbedly and it has been shown in the foregoing pages that working in this range, i.e. hot working, is effective in preventing or at least retarding this crystallization, thus imparting a smaller grain to the metal. The aggregate of ferrite and cementite existing below the range, on

the contrary, exhibits no tendency to crystallize during slow and undisturbed cooling, because this aggregate was formed and fully developed while passing through the range, the size of its elements, that is its coarseness, depending (1) upon the coarseness of the solid solution immediately before its transformation and (2) upon the time occupied in cooling through the range. Working this aggregate, therefore, as it cools to atmospheric temperature, or working it while at atmospheric temperature, i.e. cold-working steel, does not prevent its crystallization. Its effect consists in *distorting* the existing aggregate structure, chiefly through the stretching or elongation of its crystalline elements (free ferrite, free cementite, pearlite) in the direction of the forging, and such distortion in turn means decreased ductility and eventually extreme brittleness. The effect of cold working upon the structure of steel is illustrated in

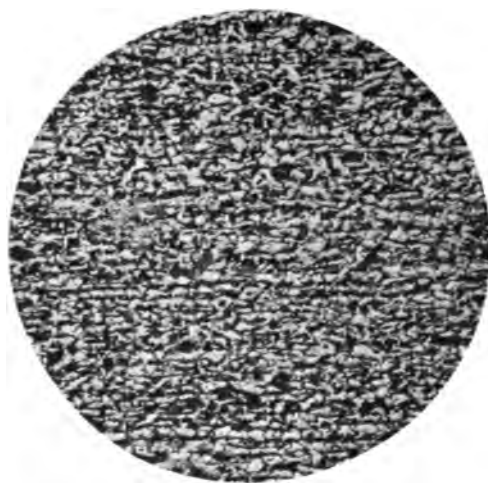


Fig. 215. — Cold-worked hypo-eutectoid steel. Carbon 0.30 per cent. Magnified 100 diameters. (Burger, Correspondence Course student.)

Figures 215 and 216 in the case of hypo-eutectoid steel. It is also depicted in the diagram of Figure 208. While the structural distortion caused by cold working is very slight near the critical range of the metal, it rapidly increases as the temperature decreases, becoming very pronounced at atmospheric temperature. The manufacture of wire by cold drawing affords a familiar instance of the effect of work performed at atmospheric temperature both on the structure and properties of the metal. It is well known that after the wire has been passed through several dies it becomes so brittle that annealing is necessary in order to make further reduction in size possible, the annealing operation removing the structural distortion and brittleness produced by working at atmospheric temperature.

The cold working of iron and steel affects deeply many of the properties of these metals, its action increasing in intensity as the temperature falls, being therefore more severe at atmospheric temperature. The elastic limit, tensile strength, and hardness are increased in a marked degree, while the ductility as represented both by elongation and reduction of area is reduced, extreme brittleness being eventually produced. It is generally believed that cold working decreases the density of iron and steel and

that the annealing of the cold worked metals increases their density. Both magnetic permeability and remanence are diminished by cold working while the coercive force is increased. Electrical resistance is slightly increased as well as the solubility of the metals in acids. The specific heat does not appear to be affected.

It has been explained in Chapter V that the straining of metals does not involve an actual distortion, an elongation for instance, of their crystalline elements, but rather a yielding through successive crystalline slips. It should also be recalled that many believe in the existence of amorphous iron produced by severe straining, as in cold working, and that the influence of that operation on some of the properties of



Fig. 216. — Cold-worked hypo-eutectoid steel. Carbon 0.30 per cent. Magnified 150 diameters. (Buck, Correspondence Course student.)

the metal, as mentioned above, may be accounted for in accordance with that hypothesis.

Mechanical Refining. — It would seem as if with the use of pyrometers at least it should be a relatively simple matter to finish steel objects very near the desirable temperature and thus secure for them the best structure that can be imparted by work alone. Upon reflection, however, it will be manifest that the problem is on the contrary an insoluble one, for the reason that unless the objects are of very small cross-sections, it is quite impossible to finish them so that their temperature will be uniform throughout, the central portions being necessarily hotter than the outside. Should the forging be so conducted that the temperature of the outside be very near the critical range, the center, being materially hotter, will coarsen on cooling, while if the implements, on the contrary, are finished so that their center may have the fine structure produced by ceasing the work at the proper temperature, their outside must necessarily suffer from cold working. The limitations of work alone as a means of imparting the best possible structure to steel are therefore quite evident.

While a uniformly fine grain cannot be imparted to steel objects of considerable size through hot working alone, the value of hot work as a means of refining the structure of steel remains very great as exemplified by the structure of properly hot-forged steel when compared with the structure of steel castings of similar composition. The finer grain imparted to steel by working it has been called by some writers "mechanical" refining to distinguish it from the refining produced by heat, i.e. from "thermal" refining. In practise hot work should be so conducted, that is, the finishing temperatures so regulated, that the central portions of the finished implements will not suffer unduly from the coarsening influence of too high a finishing temperature, while at the same time the outside will not suffer unduly from the effect of cold working. The natural tendency of rolling and other forging mills is to finish work at too high temperatures for the simple reason that the metal is then more plastic and consequently requires less power for its working. In some manufactures, however, and, especially in the rolling of rails, the importance of proper finishing temperatures has been given careful attention and the rolling operation so modified as to deliver rails of much finer grain and therefore better physical quality, than formerly.

Besides its important grain-refining influence hot work further improves the quality of steel by closing and, if the carbon be low enough, welding, the blow-holes and otherwise increasing its soundness and by removing cooling strains.

CHAPTER XV

THE ANNEALING OF STEEL

Purpose of Annealing. — The purpose of annealing steel may be (1) to increase its softness and ductility that it may, for instance, be more easily machined or (2) to secure a desirable combination of high strength and elastic limit with fair ductility that it may successfully stand the strains to which it is to be subjected. These changes of physical properties result from corresponding changes in the structure of the metal brought about by proper heat treatment. In annealing steel it is generally intended to impart to it as fine a structure, that is as small a grain, as is consistent with the nature of the treatment and the grade of the steel. Hot-forged steel objects may be improved by annealing for certain purposes, because of their structure being often (1) relatively coarse owing to high finishing temperature and (2) heterogeneous as explained in Chapter XIV.

Cold-worked steel must generally be annealed in order to increase its ductility. A large amount of cold-drawn wire, however, is used in its cold-worked condition when very high yield point and tensile strength are desired and relatively low ductility is permissible, as in spring wires, piano (music) wire, wires for wire ropes, etc., when a tensile strength exceeding 350,000 lbs. per sq. in. may be obtained.¹ Finally, steel castings have so coarse a structure as to be very deficient both in strength and ductility and should always be refined by annealing.

Nature of the Annealing Operation. — The annealing operation comprises three distinct steps: (1) heating the steel, (2) keeping its temperature constant at the annealing temperature, and (3) cooling it from the annealing to atmospheric temperature. These steps will be considered separately.

Heating for Annealing. — The first step in annealing always consists in heating the metal past its critical range because by so doing the preexisting structure, however coarse, is obliterated; the metal, for the time being, assuming a nearly amorphous structure. It is true that, as later explained, cold-drawn wire is very frequently reheated to a temperature inferior to its critical range for the purpose of removing the loss of ductility occasioned by cold working, but it may well be contended that such an operation is not, strictly speaking, annealing, for it does not imply a complete obliteration of the preexisting structure such as takes place when steel is heated past its critical range.

This important structural change is due, as we now understand it, to the passage of the steel from the state of an aggregate of ferrite and cementite to that of a homogeneous solid solution, and it is not to be wondered at that so radical a structural change should destroy effectively any preexisting crystallization. The annealing of steel castings, however, constitutes an apparent exception to the rule that

¹ The author's attention was called to these important uses of cold-worked wire in the unannealed condition by Mr. E. H. Peirce of the American Steel and Wire Co.

heating just through the range is sufficient to break up effectively the preexisting structure, for their successful annealing often requires a materially higher temperature. Should the temperature of the steel remain below its critical range, no structural change would take place and the annealing would be ineffective (I, Fig. 217) unless, indeed, in the case of cold-worked hypo-eutectoid steel when the distorted ferrite may be restored to its normal crystalline structure by heating slightly below the critical range as later explained.¹ Should, on the contrary, the temperature of the steel be carried considerably above the range, its structure, which was finest as it emerged from the range, begins to coarsen on further heating and continues to grow as the metal cools slowly to the range, so that its final structure would be at least

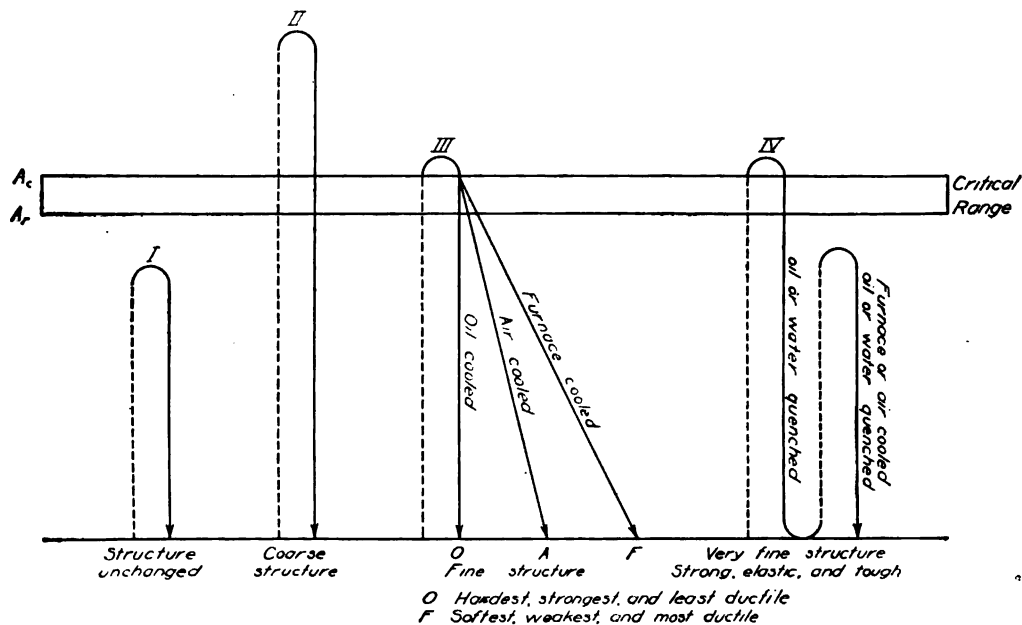


Fig. 217. — Diagram depicting the annealing of steel.

relatively coarse (II, Fig. 217). Clearly, therefore, to anneal steel forgings they should be heated through their critical range and kept at a temperature as close to the upper part of that range as possible (III, Fig. 217). The annealing temperature will, of course, vary with the carbon content since the position of the critical range, or rather its width, varies likewise. The structural refining taking place in heating through the critical range is strikingly illustrated by Stead in Figure 218, which shows coarsely crystalline soft steel heated at one end to above 900 deg. C. The refined portion was heated above the critical range. The sharp demarcation between the original coarse structure and the fine structure produced by annealing should be noted.

¹ When steel contains hardening carbon, it may be softened and made more ductile by heating it to temperatures lower than its critical range (as in the tempering of hardened steel), but such treatment is not, or at least should not be, called annealing. Cooling strains may also be removed, at least in part, by heating below the range.

The following ranges of temperatures are recommended by the Committee on Heat Treatment of the American Society for Testing Materials. The report of the Committee states that for steels containing more than 0.75 per cent manganese slightly lower temperatures suffice.

RANGE OF CARBON CONTENT	RANGE OF ANNEALING TEMPERATURE
Less than 0.12 per cent	875 to 925 deg. C. (1607–1697 deg. F.)
0.12 to 0.25 per cent	840 to 870 deg. C. (1544–1598 deg. F.)
0.30 to 0.49 per cent	815 to 840 deg. C. (1499–1544 deg. F.)
0.50 to 1.00 per cent	790 to 815 deg. C. (1454–1499 deg. F.)

The proper temperatures to which to heat carbon steels of ordinary commercial quality for the purpose of annealing as well as of hardening are indicated graphically in Figure 219 for various percentages of carbon.

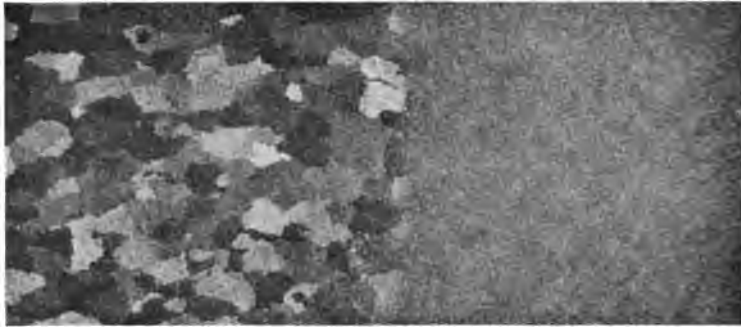


Fig. 218. — Coarsely crystalline soft steel heated at one end to above 900 deg. C. (Stead.)

Time at Annealing Temperature.—The steel object should be kept at the annealing temperature long enough to be heated right through to that temperature. The Committee on Heat Treatment, referred to above, states that an exposure of one hour should be long enough for pieces twelve inches thick. Thicker pieces, of course, need a longer heating.

The usefulness of pyrometers in conducting annealing operations is obvious. Their use is to be strongly recommended.

Cooling from Annealing Temperature. — Having imparted a fine structure to the steel the next step must be to retain it. The most effective way of accomplishing this consists in cooling the steel very quickly, by quenching it in water for instance, as time is then denied for the structure to coarsen at all while the metal cools to atmospheric temperature. Such rapid cooling, however, as is well known, hardens the metal and deprives it of ductility (unless, indeed, it contains very little carbon), and this would defeat the purpose of annealing which always demands the retention of considerable ductility. It follows from these considerations that, in annealing, cooling from the annealing temperature cannot be so rapid as to very materially harden the steel.¹ Its rate should, moreover, be regulated in accordance with the kind of

¹ Unless the double treatment presently to be described is resorted to.

properties we most desire the steel object to possess. For instance, (1) if softness and ductility are wanted (for ease in machining), necessarily at a certain sacrifice of strength and elasticity, the cooling should be very slow, to wit, with the furnace in which the object was heated, (2) if greater hardness (for wearing power), strength, and elasticity are desired, at the necessary sacrifice of some ductility, the cooling should be more rapid as, for example, in air or, in the case of low carbon steel, in oil or, with very low carbon steel, even in water (III, Fig. 217).

Rate of Cooling vs. Carbon Content. — The lower the carbon content the more rapid may be the cooling from the annealing temperature without affecting too deeply

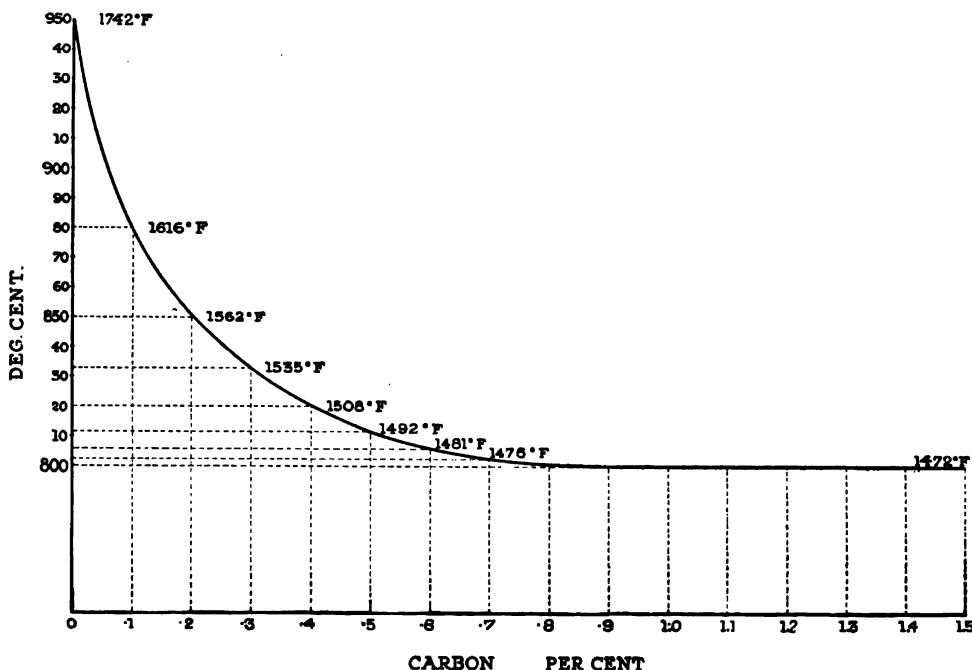


Fig. 219. — Diagram showing suitable temperatures for annealing (and hardening) carbon steel forgings.

the ductility of the metal. For instance, (1) steel containing not over 0.15 per cent carbon may be quenched in water, thereby increasing its strength and elastic limit and still remain very ductile, (2) steel with less than 0.20 or 0.30 per cent carbon may be quenched in oil with satisfactory results, (3) with a larger proportion of carbon such rapid cooling is no longer possible, as it would destroy the ductility of the metal, recourse having then to be had to cooling in air for the desired combination of strength and ductility or to the double annealing treatment soon to be described.

Rate of Cooling vs. Size of Object. — Since large objects necessarily cool more slowly than smaller ones when subjected to the same cooling influences, it is evident that the external conditions should also be regulated in accordance with the dimensions of the objects treated. To secure maximum softness and ductility, for instance, the cooling of small objects should be more effectively retarded than the cooling of

larger ones. Assume, for example, two objects made of the same steel, one large and one small, and both cooled in air from the annealing temperature; the smaller object will be harder and less ductile than the larger one, because of its quicker cooling. To render it as soft and ductile as the larger object cooling in the furnace may be necessary. Similarly, to give strength and high elastic limit the cooling of large objects must be more vigorously hastened than that of smaller objects as, for instance, cooling in oil against cooling in air for the smaller piece.

Furnace Cooling from Annealing Temperature. — As an example of the effect of furnace cooling upon the structure of steel, let us take a steel bar $\frac{1}{2}$ inch square, containing 0.50 per cent carbon, heated to 1000 deg. C. and slowly cooled with the furnace. Its structure is shown in Figures 220 and 221. It will be seen to be composed



Fig. 220. — Steel. Carbon 0.50 per cent. Magnified 100 diameters. Heated to 1000 deg. C. and slowly cooled in furnace. (R. W. Smyth in the author's laboratory.)

of the normal proportions of pearlite and free ferrite, namely, some 60 per cent of the former, and it will also be noted that the pearlite is distinctly laminated (Fig. 221), and that in places at least the ferrite forms characteristic polyhedral grains. This structure is due to the slow cooling of the steel through its critical range, which permits the rejection of the full amount of free ferrite and a distinct crystallization of the constituents of the residual austenite into plates of ferrite and cementite. The relative softness and great ductility of the steel in this condition is due (1) to the presence of the full amount of soft ferrite in relatively large areas and (2) to the presence of distinctly laminated pearlite indicating the absence of hardening carbon as explained later.

Air Cooling from Annealing Temperature. — To illustrate the influence of air cooling upon the structure of steel, let us take likewise a steel containing some 0.50 per cent carbon, heated to 1000 deg. C. and cooled in air. Its structure is shown in

Figure 222. It will be found quite unlike the structure of the same steel after furnace cooling (Figs. 220 and 221). It contains a much smaller proportion of free ferrite, apparently not over 20 per cent, in the form of a distinct net surrounding dark meshes which a high magnification fails to resolve into distinct parallel plates. Relatively quick cooling through the critical range has prevented the separation of the normal amount of free ferrite, from which it necessarily follows that the dark constituent contains more ferrite than true pearlite; nor has it the structure of true pearlite, time also having been denied on cooling through the range for the formation of distinct plates of ferrite and cementite. Sorbite is the name of this constituent. The structure of pearlite passing into sorbite is shown in Figure 223.

Properties of Sorbite. — Sorbite has already been briefly described in Chapter XIV, where it was shown that it could be produced in steel forgings of small sections

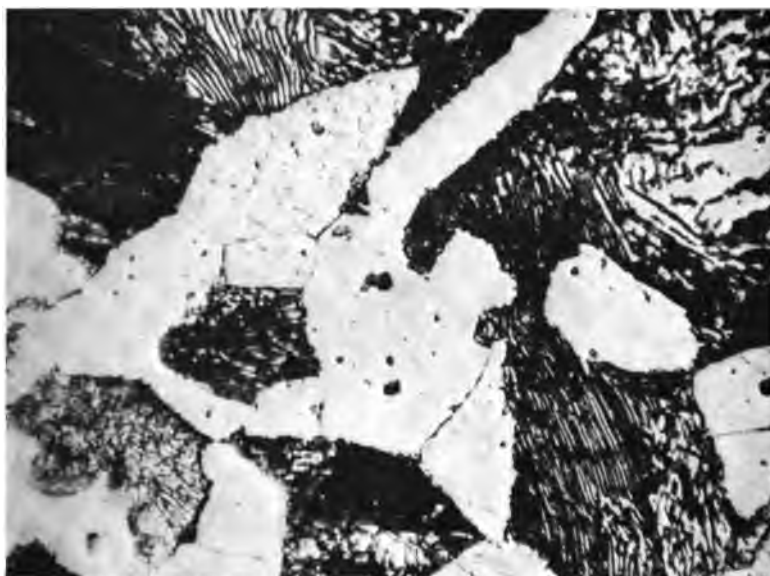


Fig. 221. — Steel. Carbon 0.50 per cent. Magnified 670 diameters. Heated to 1000 deg. C. and slowly cooled in furnace. (C. C. Buck, Correspondence Course student.)

through simple air cooling from a finishing temperature superior to the critical range, and in larger sections by hastening somewhat their cooling through that range. It has also been stated that sorbite is harder, stronger, and less ductile than pearlite. By so regulating the cooling from the annealing temperature, therefore, that sorbitic steel is produced, hardness, strength, and elasticity will be promoted at the sacrifice of some ductility (III, Fig. 217). It will be explained in another chapter that sorbite is generally regarded as one of the transition stages assumed by the metal as it passes from its austenitic condition, stable above the critical range, to its pearlitic condition, stable below that range.

Influence of Maximum Temperature. — The influence of the maximum temperature to which steel is heated before being allowed to cool is well shown in Figures 224 to 227 which should be compared with Figures 220 to 223. They refer to steel

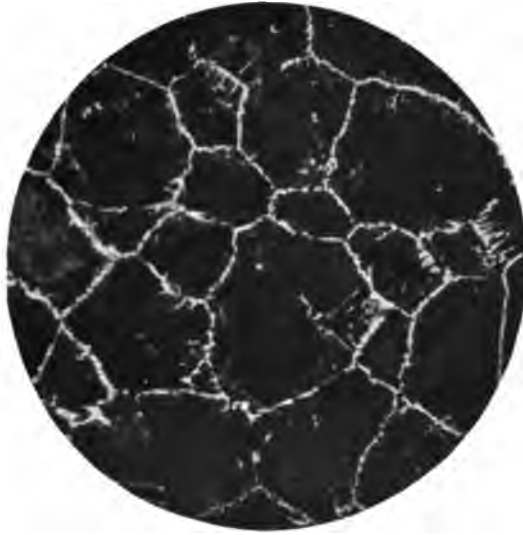


Fig. 222. — Steel. Carbon 0.50 per cent. Magnified 100 diameters. Heated to 1000 deg. C. and cooled in air. (Boynton in the author's laboratory.)

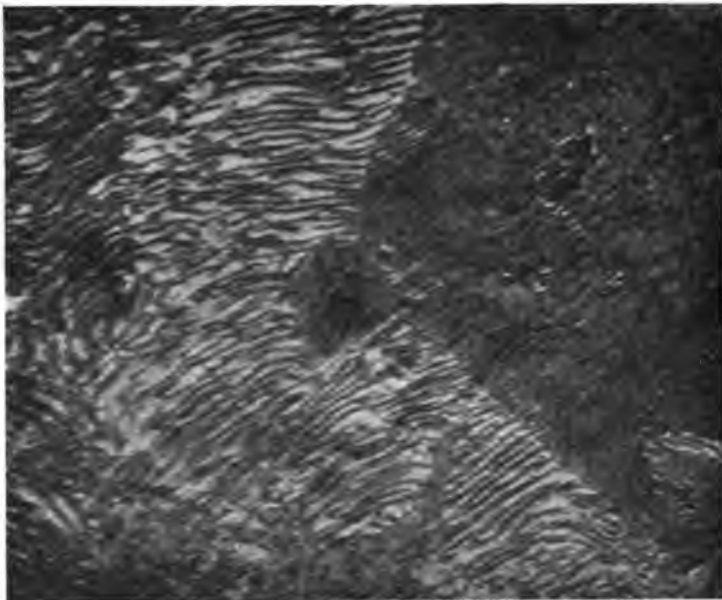


Fig. 223. — Steel. Carbon 1 per cent. Magnified 1500 diameters. Pearlite (laminated) passing into sorbite. (Osmond.)

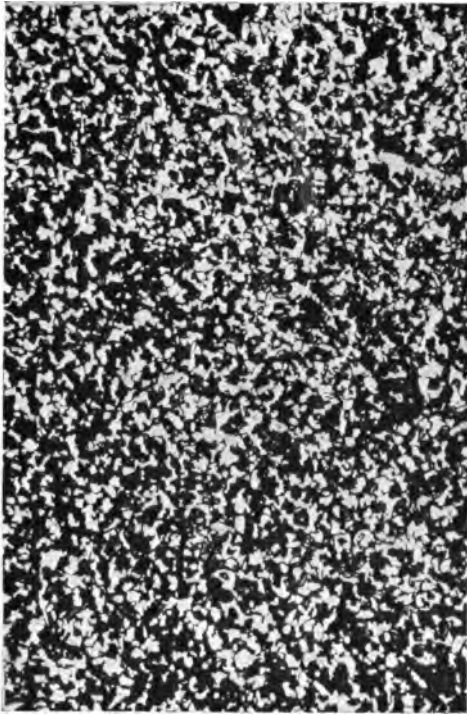


Fig. 224. — Magnified 100 diameters. Heated to 800 deg. C. and slowly cooled in furnace.

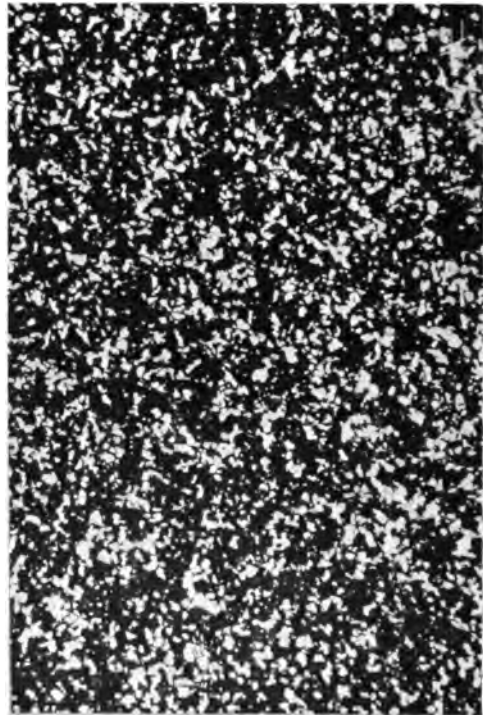


Fig. 225. — Magnified 100 diameters. Heated to 800 deg. C. and cooled in air.

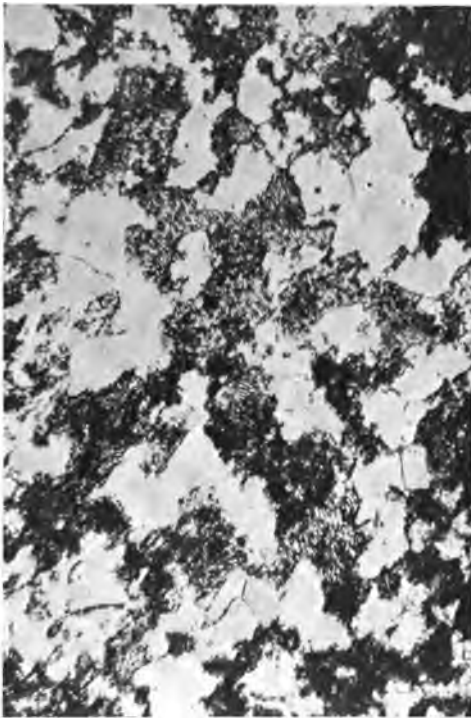


Fig. 226. — Magnified 670 diameters. Heated to 800 deg. C. and slowly cooled in furnace.

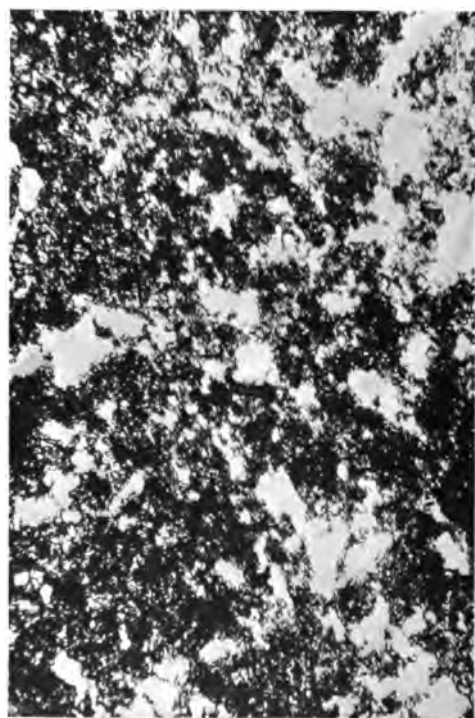


Fig. 227. — Magnified 670 diameters. Heated to 800 deg. C. and cooled in air.

Figs. 224-227. — Steel. Carbon 0.50 per cent. (C. C. Buck, Correspondence Course student.)

containing 0.50 per cent carbon and heated to 800 deg. C., while the structures illustrated in Figures 220 to 223 refer to the same steel but heated to 1000 deg. The constituents are the same, namely, ferrite and pearlite in the furnace-cooled samples, ferrite and sorbite in the air-cooled samples, but the higher temperature resulted in the formation of larger particles of pearlite or sorbite, evidently because of the formation above the critical range of larger austenitic grains.

Influence of Time at Maximum Temperature. — Maintaining steel for a long time at a high temperature causes the formation of large austenite grains, which in passing through the range are converted into large pearlite or sorbite grains with

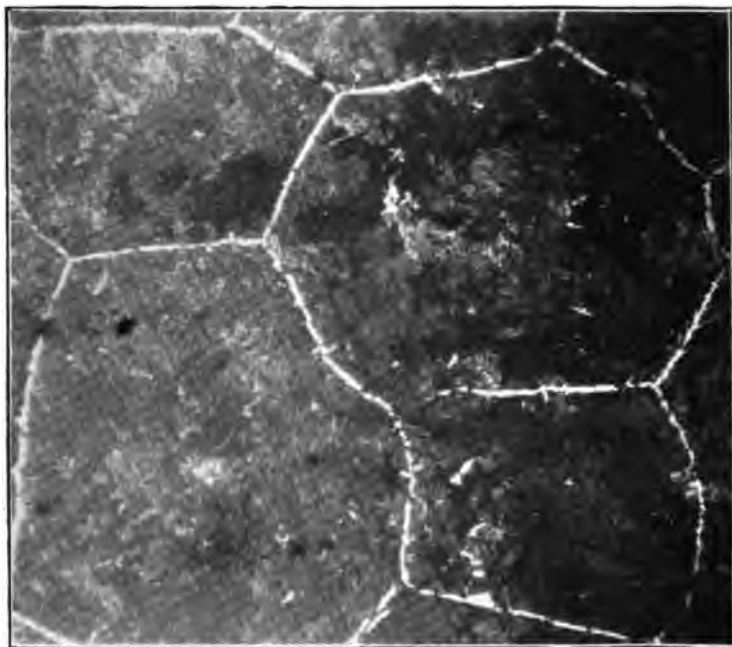


Fig. 228. — Steel. Carbon 0.50 per cent. Magnified 100 diameters. Heated to 1150 deg. C. for two hours and cooled in air. (Boynton in the author's laboratory.)

rejection of free ferrite in hypo-eutectoid steel and of free cementite in hyper-eutectoid steel. It is also noted that the more prolonged the heating the smaller the amount of the excess constituent (free ferrite or free cementite) separating on rapid (air) cooling through the range. This is shown in Figure 228 in which is depicted the structure of steel containing 0.50 per cent carbon heated to 1150 deg. C. for two hours and air cooled. The very large sorbitic grains should be noted as well as the very small proportion of free ferrite.

Oil and Water Quenching from Annealing Temperature. — As already explained only steel containing very little carbon may be quenched in oil or water for purposes of annealing, unless, indeed, the double treatment soon to be described be employed when higher carbon steels may be so quenched. The structure of steel containing 0.10 per cent carbon, heated to 950 deg. C. and quenched in water, is shown in Figure 229 while in Figure 230 is seen the structure of steel containing 0.20 per cent carbon

quenched in oil from a temperature of 850 deg. C. Rapid cooling through the range did not prevent the separation of the bulk of the large amount of excess ferrite present in these steels, hence their softness and ductility even after quenching. They are, however, somewhat stronger and more elastic than similar steels more slowly cooled, (1) because they contain a somewhat smaller proportion of soft free ferrite, (2) because the free ferrite they contain has crystallized into smaller grains, and (3) because their carburized constituent is sorbitic or even martensitic¹ rather than pearlitic.

Double Annealing Treatment. — It has been stated that the most effective way of retaining in the cold the very fine structure acquired by steel in passing through its critical range consisted in cooling it very rapidly as soon as it emerged from that range, as for instance by quenching it in water. This treatment, however, unless the metal contains very little carbon, hardens the steel and deprives it of ductility, whereas



Fig. 229. — Steel. Carbon 0.10 per cent. Magnified 100 diameters. Heated to 950 deg. C. and quenched in water. (Boylston.)



Fig. 230. — Steel. Carbon 0.20 per cent. Magnified 100 diameters. Heated to 850 deg. C. and quenched in oil. (Boylston.)

annealed steel should not be very hard and should possess much ductility. If this fine-grained but hard steel, however, be reheated to a temperature close to but below its critical range, say to from 500 to 650 deg. C., it loses its hardness but retains its fine structure and again becomes ductile (IV, Fig. 217).

The double treatment outlined above fulfils admirably the aims generally sought in annealing, namely, the production of a very fine structure possessing high strength and elastic limit with fair ductility, in other words toughness and high resistance to wear, to shock, and to fatigue. The change of structure taking place on heating hardened steel close to the lower limit of its critical range will be considered at some length in Chapter XVII. It will suffice to note here that the metal passes from a fine martensitic or troostitic condition (the ordinary condition of well-hardened steel) to an equally fine sorbitic condition, possessing in a high degree the physical properties

¹ Martensite is the ordinary constituent of steel hardened by quenching. It is hard and deprived of ductility.

desired. The first heating is sometimes called "grain refining" treatment and the second "toughening" treatment.

The quenching of a piece of steel from above its critical range, while simple enough in the case of very mild steel, presents increasing difficulties as the carbon increases. It should be conducted with care and intelligence and only by experts. Steel containing but little carbon, say not over 0.30 per cent, may be quenched in water, others should be quenched in oil. The Committee on Heat Treatment of the American Society for Testing Materials recommends, in order to lessen the danger of

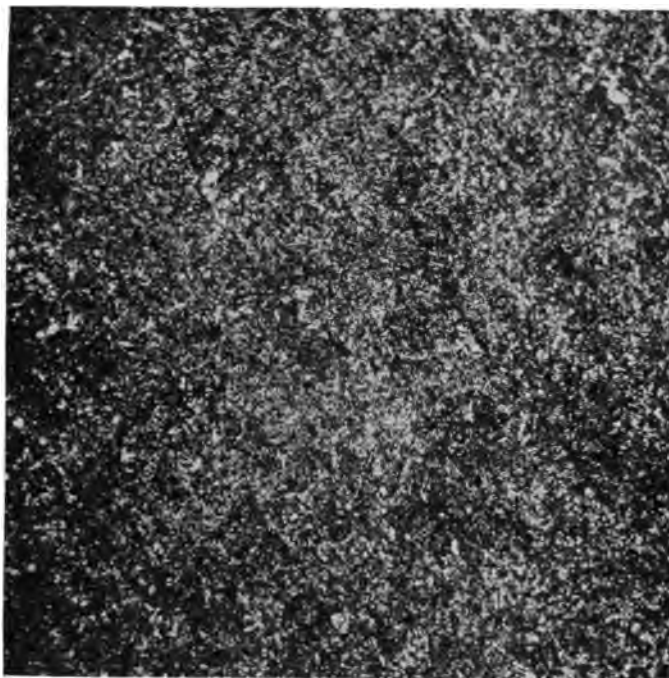


Fig. 231. — Steel. Carbon 0.50 per cent. Magnified 150 diameters. Heated to 850 deg. C., quenched in water, reheated to 600 deg., and cooled in air.

cracking, that the object be removed from the oil or water bath before its temperature has fallen below 160 deg. C., or in any event below 100 deg., and that the second treatment be applied within a few hours after the quenching, preferably without ever allowing the piece to cool below 100 deg. and certainly not below 20 degrees. The final properties of the steel will depend upon the temperature of the second heating; the higher that temperature the softer and more ductile will it be, but also the less strong and elastic. For great strength, high elastic limit, and little ductility reheating to 400 or 500 deg. should be applied, while for great ductility, at the sacrifice of considerable strength, the reheating should be carried to some 700 deg. For intermediate tensile strength, elastic limit, and ductility such as are desired in the majority of cases, the temperature of the second treatment should be between 550 and 650 deg. C. While from purely theoretical considerations it might be argued that the rate of cool-

ing from this second treatment is immaterial, there is little doubt but that the strength of the steel increases somewhat and its ductility decreases with the rapidity of cooling. This cooling may be performed in the furnace, in air, in oil, or in water.

The double annealing treatment described in the foregoing paragraphs was first suggested by Wallerant of the Creusot Steel Works, France. It was also described by André Le Chatelier and adopted by the French navy. Its use is now general when high physical requirements are to be met.

In Figure 231 is shown the structure of steel, containing some 0.50 per cent carbon, after double annealing. The fineness of the structure should be noted as well as the

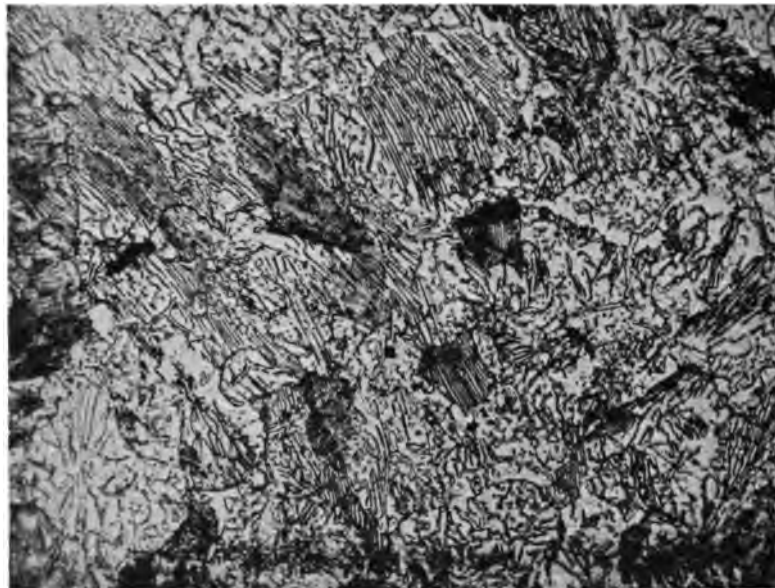


Fig. 232. — Steel. Eutectoid. Magnified 412 diameters. Heated to 800 deg. C. and slowly cooled in furnace. (C. C. Buck, Correspondence Course student.)

lack of laminations and the absence of free ferrite. This steel is composed wholly of finely divided sorbite.

Annealing Eutectoid Steel. — While the mechanism of the structural changes taking place on annealing steel has been made clear in the preceding pages, it may not be without interest to consider further and in succession the annealing of eutectoid, hypo-eutectoid, and hyper-eutectoid steel, as these three types of steels have different structures and their annealing involves different structural changes.

Slowly cooled eutectoid steel is composed wholly of pearlite which, upon being heated through the single critical point of the metal, namely $Ac_{3.2.1}$, is converted into a solid solution (austenite). The grains of this austenite are very fine as the steel emerges from its range and they are kept from growing by preventing the steel from reaching a higher temperature. On cooling through $Ar_{3.2.1}$ the metal again becomes pearlitic if it be given time, as for instance in cooling in the furnace, while it becomes sorbitic if cooled more quickly, as for instance in air in the case of small objects.

Should the steel be quenched in water or oil from the annealing temperature and then reheated near but below the point $Ac_{3.2.1}$, the finely martensitic-troostitic structure produced by quenching from above the range is converted into very fine sorbite.

It has been explained in Chapter XIII that, for like treatments, the structure of eutectoid steel is finer than that of either hypo-eutectoid or hyper-eutectoid steel and this holds true in the case of annealed samples, although the difference may not be noticeable when comparing the structure of eutectoid steel with that of hyper-eutectoid steel containing but a slight excess of free cementite.

In Figure 232 is shown the structure of eutectoid steel heated to 800 deg. C. and slowly cooled in the furnace. It is made up of well-developed pearlite. The struc-



Fig. 233. — Steel. Eutectoid. Magnified 720 diameters. Heated to 825 deg. C., quenched in oil, reheated to 650 deg., and cooled in air. (Boylston.)

ture of the same steel, quenched in oil at 825 deg., reheated to 650 deg., and cooled in air, is exhibited in Figure 233. The metal is now composed of fine-grained sorbite.

Annealing Hypo-Eutectoid Steel. — Slowly cooled hypo-eutectoid steel is an aggregate of pearlite and free ferrite. On being heated through its critical range, as soon as the point Ac_1 is reached, the pearlite is bodily converted into austenite, while the ferrite still remains free. On further heating, however, it begins to be absorbed by austenite, its absorption being completed as the metal emerges from its Ac_3 point. Above Ac_3 the steel is composed wholly of homogeneous austenite. On cooling through the critical range unless, indeed, the cooling be very rapid and sufficient carbon be present, ferrite is again liberated in amount proportional to the slowness of the cooling up to the maximum quantity consistent with the carbon content in the steel. If the cooling be very slow then, for instance in the furnace, the totality of the excess ferrite will be rejected and the residual austenite converted into well-defined pearlite (Figs. 221 and 226), while if the cooling be more rapid, for instance in air in the case of small objects or in oil with larger ones, a portion only of the excess

ferrite is liberated while the residual austenite is converted into sorbite (Figs. 222 and 227). The liberation of ferrite taking place during the slow cooling of hypo-eutectoid steel coarsens its structure and is the chief reason why annealed hypo-



Fig. 234. — Steel. Hypo-eutectoid. 0.20 per cent carbon. Annealed. Magnified 100 diameters. (W. J. Burger, Correspondence Course student.)

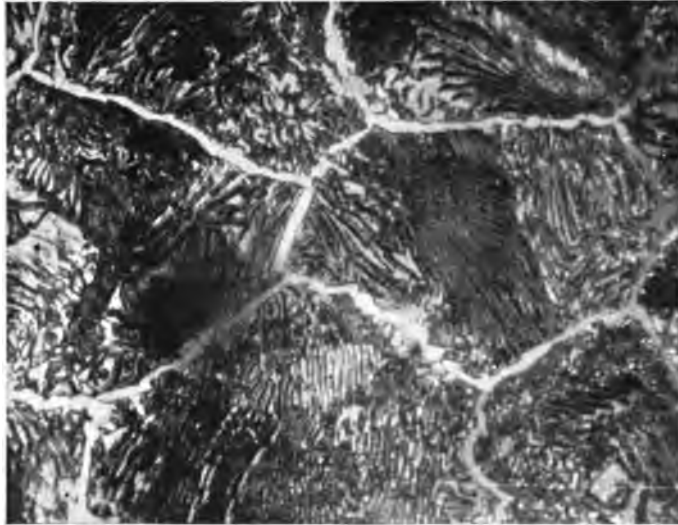


Fig. 235. — Steel. Carbon 1.43 per cent. Magnified 500 diameters. Heated above critical range and slowly cooled in furnace. (Boyn-ton in the author's laboratory.)

eutectoid steel cannot have as fine a structure as annealed eutectoid steel. Howe further contends that as hypo-eutectoid steel is heated from A_{c1} to A_{c3} a new crystalline growth takes place which is the coarser the greater the distance between A_1 and

A_3 , that is the less carbon in the steel, so that by the time the old structure has been obliterated, i.e. at Ac_3 , a new grain has formed which is an additional reason why the structure of hypo-eutectoid steel cannot be refined to the same extent as that of eutectoid steel.

The structure of hypo-eutectoid steel after double annealing has been shown in Figure 231. The rapid cooling through the range prevented the liberation of ferrite, while the second treatment produced sorbite, but this sorbite is not as fine grained as that produced in eutectoid steel by similar treatment.

An additional illustration of the fine structure that can be imparted to hypo-eutectoid steel by annealing is given in Figure 234 in the case of steel containing 0.20 per cent carbon.

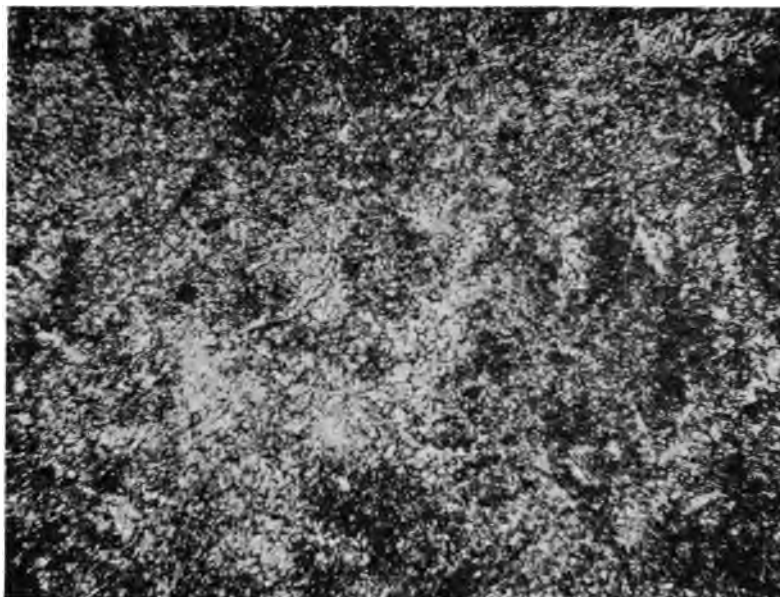


Fig. 236. — Steel. Carbon 1.25 per cent. Magnified 670 diameters. Heated to 800 deg. C. and quenched in oil, reheated to 600 deg. and air cooled. (C. C. Buck, Correspondence Course student.)

Annealing Hyper-Eutectoid Steel. — Slowly cooled hyper-eutectoid steel is an aggregate of pearlite and free cementite. On heating it through its critical range, i.e. through its $Ac_{3.2.1}$ and Ac_{cm} points, pearlite is converted into austenite at the lower point and this austenite absorbs the free cementite as the metal is further heated from $Ac_{3.2.1}$ to Ac_{cm} . At Ac_{cm} the absorption is complete and the metal composed entirely of austenite. On cooling through the range, if time be given, as for instance in cooling in the furnace, the full proportion of free cementite is again liberated and the residual austenite converted at $Ar_{3.2.1}$ into clearly laminated pearlite (Fig. 235). If the cooling be more rapid, as for instance in cooling small pieces in air, a portion only of the free cementite is set free, while the residual austenite is converted into sorbite. This setting free of cementite, like the liberation of ferrite in hypo-eutectoid steel, coarsens the structure. The coarsening influence of free cementite, how-

ever, is far from being as marked as that of free ferrite, chiefly because free cementite is generally present in much smaller proportions. Steel containing as much as 1.50 per cent carbon, for instance, contains but 11.50 per cent of coarsening cementite, while steel with 0.40 carbon contains 52 per cent of coarsening ferrite.

In Figure 236 is shown the structure of hyper-eutectoid steel subjected to the double annealing treatment, which resulted in the production of fine-grained sorbite.

For the purpose of annealing hyper-eutectoid steel, it is seldom advisable to heat it much above its lower critical point $Ac_{3.2.1}$, because while at Ac_{cm} the free cementite would be completely reabsorbed and, through relatively quick cooling, could be prevented, to a certain extent at least, from again separating, the coarseness of structure resulting from so high a temperature would generally more than offset the gain resulting from the presence of a smaller proportion of free cementite.



Fig. 237. — Steel wire. 0.08 per cent carbon. Cold drawn. Magnified 100 diameters. (E. H. Peirce.)



Fig. 238. — Steel wire. 0.08 per cent carbon. Cold drawn and reheated below its critical range. Magnified 100 diameters. (E. H. Peirce.)

Annealing of Cold-Worked Steel. — It has already been mentioned that the cold working of steel, that is, the application of severe compression or tension when its temperature is below its critical range, and more specifically at atmospheric temperature, results in a marked distortion of its structural elements, a decided elongation for instance if the steel is subjected to tension as in wire drawing (Fig. 237, also Figs. 215 and 216, Chapter XIV), and that such distortion causes a great increase of tenacity and hardness but that it lowers the ductility decidedly, eventually producing brittleness. It has also been stated that many other properties of steel are deeply affected and that this action of cold working is ascribed by some to the formation of a certain amount of amorphous iron (Chapter XIV).

When it is desired to increase the ductility of cold-worked steel in order that it may be subjected to additional drafting or because the uses to which it is to be put call for greater ductility and softness, the metals should be subjected to suitable heat treatment. In the case of cold-worked hypo-eutectoid steel which is composed of elongated particles of ferrite and pearlite it is sufficient in order to restore its duc-

tility to heat it to a temperature varying between 550 and 600 deg. C. and, therefore, considerably below its critical range (see Fig. 238). This is especially so when the carbon content does not exceed 0.40 per cent and when therefore the metal contains a large amount of free ferrite. It has been stated by some that 520 deg. C. marks the temperature which should be reached in order to produce the desired results in very low carbon steel. This heating of cold worked steel below the critical range to increase its ductility is sometimes called at the works "process" or "works" annealing (J. T. Tinsley). The treatment causes the free ferrite to recrystallize in its normal polyhedral pattern (Fig. 238) or, if we believe in the existence of amorphous iron in cold-worked steel, the return of that amorphous iron to the crystalline condition and hence decreased hardness and strength and increased ductility. It should be noted, however, that the elongated particles of pearlite remain elongated (Fig. 238), the



Fig. 239. — Steel wire. Cold drawn and reheated above its critical range. Magnified 100 diameters. (Boylston.)



Fig. 240. — Patented steel wire. 0.85 per cent carbon. Magnified 1000 diameters. (E. H. Peirce.)

ferrite particles alone being affected by the treatment. When maximum softness is required the cold-worked steel must be annealed by heating it above its critical range followed by slow cooling. This treatment, of course, removes the distortion of the pearlite as well as of the ferrite (Fig. 239) since both constituents above the critical range form a homogeneous solid solution. In wire mills this is known as "dead soft" annealing (Tinsley.)

When it is desired to produce wires having a very high yield point and very great tenacity (300,000 to 400,000 lbs. per sq. in.) while retaining considerable toughness, the heat treatment is so conducted as to produce sorbite to the practical exclusion of pearlite, free ferrite, or free cementite, and is generally applied to steel wires containing some 0.35 to 0.85 per cent carbon (Tinsley). The process is known as "patenting" and the product as "patented" wire. To produce sorbite the cooling through the critical range should be relatively rapid but not so rapid as to cause the retention of martensite or even troostite lest the steel be brittle, nor should it be slow enough to permit the formation of pearlite since this would imply decreased tenacity. According to Tinsley, patenting in practice is usually conducted as a continuous

operation, the wire being led through the heated tubes of a furnace and cooled by being brought into the air or into a bath of molten lead comparatively cool but seldom below 700 deg. F. (367 deg. C.). The structure of patented wire is shown in Figure 240.

Tinsley writes that by a proper combination of drafting and patenting it is possible to obtain music wire from a 0.70 per cent carbon steel which will have a tensile strength of 400,000 lbs. per sq. in., and be sufficiently tough to be wrapped about itself without breaking and be swaged flat to one half its original thickness without splitting. The same author also states that although it might at first be supposed that wire annealed to a pearlitic condition because of its greater softness and ductility should withstand drafting to a greater extent than patented (sorbitic) wire the facts



Fig. 241. — Steel. Cast. Carbon 0.30 per cent.
Magnified 100 diameters. Annealed. (W. J.
Burger, Correspondence Course student.)

are that owing to the rapid loss of ductility characteristic of a pearlitic structure it will not withstand drawing to anywhere near the same degree as will the patented structure.

Annealing Steel Castings. — It has been mentioned that the very coarse structure of steel castings, called "ingotism" by Howe, was not as readily refined as the structure of steel forgings, its satisfactory annealing often necessitating prolonged heating slightly above the range or short heating to temperatures considerably higher than the critical range. Notwithstanding their greater resistance to the annealing treatment, successfully annealed castings may possess physical properties fairly equal to those of forgings. In Figure 241 is shown the structure of cast steel containing some 0.30 per cent of carbon and properly annealed. The presence of a relatively small amount of free ferrite will be noted. When highly magnified the carbon-holding constituent should have a sorbito-pearlitic appearance.

The Committee on Heat Treatment of the American Society for the Testing of Materials recommends, for the purpose of annealing, heating carbon-steel castings



Fig. 242. — Cast condition.

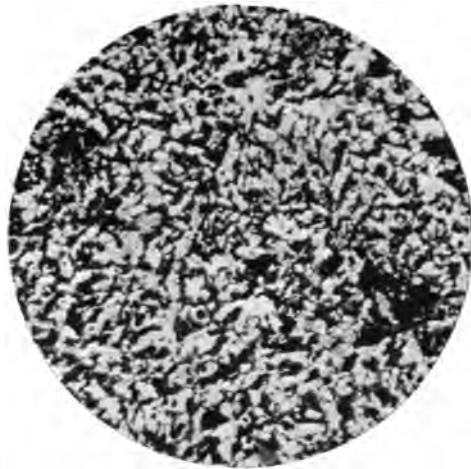


Fig. 243. — Heated to 875 deg. C. and furnace cooled.

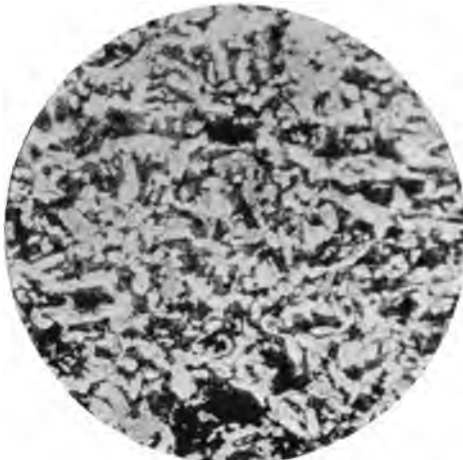


Fig. 244. — Heated to 875 deg. C. for five hours and air cooled.

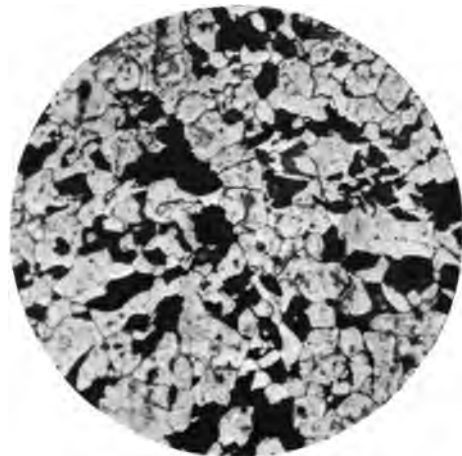


Fig. 245. — Heated to 875 deg. C. and air cooled.

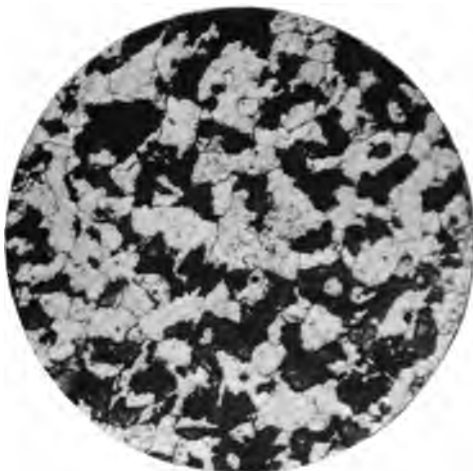


Fig. 246. — Heated to 1100 deg. C. and air cooled, reheated to 875 deg. C. and air cooled.

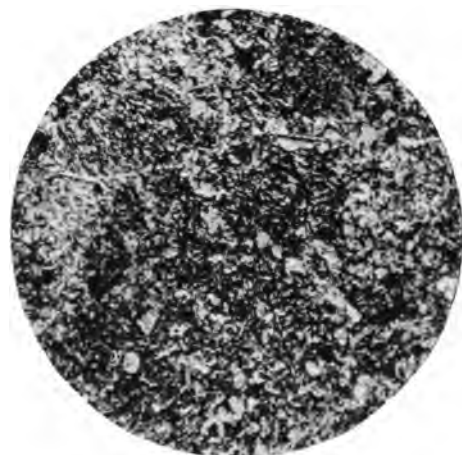


Fig. 247. — Heated to 875 deg. C. and quenched in water, reheated to 660 deg. C. and quenched in oil.

Annealing of cast steel containing 0.30 per cent carbon. All photomicrographs are magnified 100 diameters. (R. S. Simmons in the author's laboratory.)

slowly and uniformly to temperatures varying with the carbon content of the steel approximately as follows:

CARBON PER CENT	TEMPERATURES DEG. C.
Up to 0.16	925
0.16 to 0.34	875
0.35 to 0.54	850
0.55 to 0.79	830

The castings should be kept at the maximum temperature a sufficient length of time to ensure the refining of the grain. The castings should be cooled (1) slowly and uniformly in the furnace when it is desired that the steel shall possess the maximum softness and (2) at an accelerated rate, when it is desired that the steel possess rather higher tensile strength and elastic limit.

The rather long annealing indicated above may be replaced by heating the castings to some 1200 deg. C. for a few minutes, cooling in the air, and reheating to a temperature slightly above $Ac_{3.2.1}$, $Ac_{3.2}$, or Ac_1 (J. H. Hall).

The double treatment used with such satisfactory results in annealing steel forgings may also be applied to castings and is strongly recommended by Hall, especially when it is desired to develop high resistance to shock, maximum strength, and elastic limit. From the first heating which should be but slightly above $Ac_{3.2.1}$, $Ac_{3.2}$ or Ac_1 the castings, if their carbon content and shape permit it, should be quenched in water, or if too high in carbon or of such shape as to lead to cracking, in oil. They should then be reheated to from 640 to 680 deg. C. for 2 to 8 hours, in order to convert any martensite or troostite into sorbite and to relieve cooling stresses. If the carbon content, size, and shape of the castings are such that there is danger of cracking when quenched in water or even in oil, they should be cooled in air or in an air blast and reheated to from 660 to 720 deg. C. to relieve cooling stresses. If the castings are cooled in oil or in water it is best to remove them from the quenching baths before they have become cold and they should not be placed in a hot furnace or reheated rapidly when put in a cold furnace.

The structures imparted to cast steel containing 0.30 per cent carbon (Fig. 242) by various annealing treatments are illustrated in Figures 243 to 247.

Rate of Cooling vs. the Structure of Steel. — An attempt has been made in Figures 248 and 249 to illustrate graphically the mechanism of the very great influence exerted upon its structure and physical properties by the speed with which steel cools through its thermal critical range. Steel containing some 0.30 per cent carbon has been selected but the same reasoning would apply to any other hypo-eutectoid steel as well as to hyper-eutectoid steel. In the latter case, however, free cementite instead of ferrite would form, if time be given, in cooling through the range.

It is shown in Figure 248 that while the steel above its critical range is composed entirely of austenite and while, after very slow cooling, it contains nothing but ferrite and pearlite, in passing through the range the transformation of the solid solution austenite into the ferrite-pearlite aggregate is not sudden but gradual, several transition constituents being formed, namely martensite, troostite, and sorbite. Sorbite has already been described while the nature of martensite and troostite will be discussed in the next chapter. It follows as indicated in Figure 248 that various types of structures are produced theoretically at least while steel cools through its

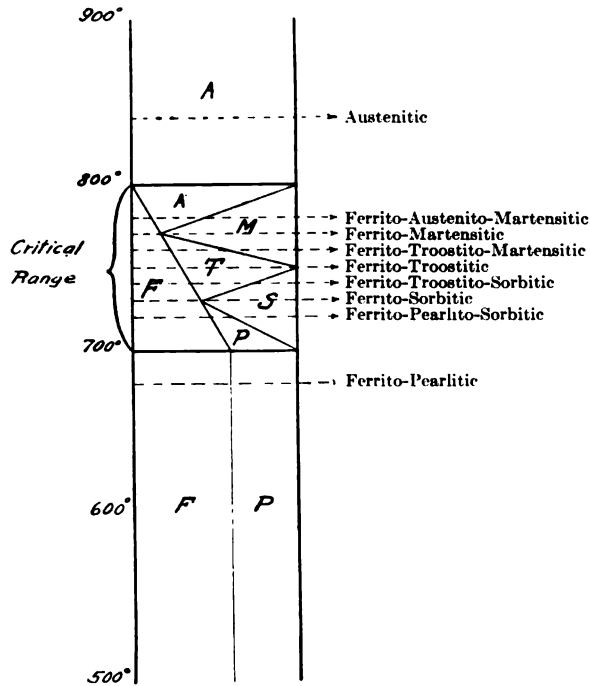


Fig. 248. — Diagram depicting the mechanism of the structural transformation in steel containing 0.30 per cent carbon on slow cooling through the critical range.

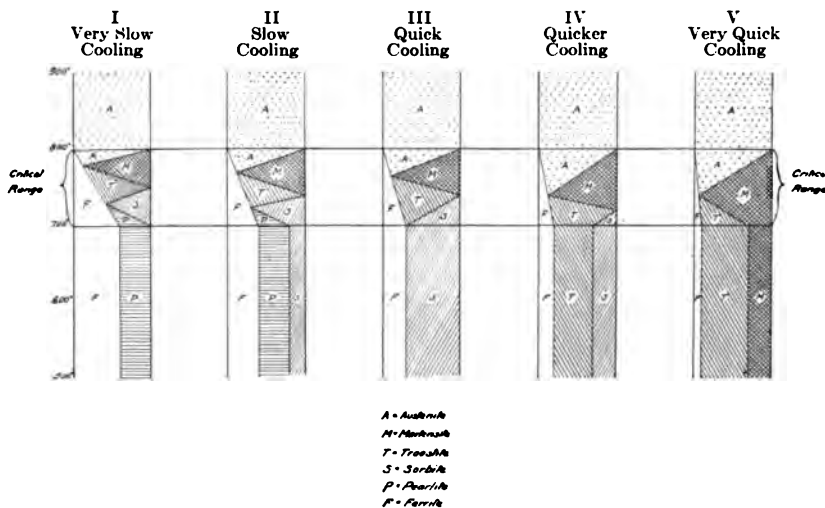


Fig. 249. — Diagram depicting the influence of the rate of cooling on the mechanism of the structural transformation taking place in the critical range in steel containing 0.30 per cent carbon.

critical range, containing besides free ferrite either (1) austenite and martensite, (2) martensite alone, (3) martensite and troostite, (4) troostite alone, (5) troostite and sorbite, (6) sorbite alone, or (7) sorbite and pearlite.

In Figure 249 it is intended to depict the possibility of retaining in the cold, through suitable regulation of the cooling, these various structures and, therefore, the possibility by this means of imparting to steel many different physical properties. As cooling is accelerated, first some sorbite is retained together with pearlite, then in succession, sorbite alone, sorbite and troostite, etc., while the amount of free ferrite separating decreases. The metal, therefore, becomes stronger, harder, and less ductile (1) because of a diminishing proportion of soft, ductile ferrite and (2) because of tenacious but moderately ductile sorbite replacing weaker but more ductile pearlite. The presence of troostite and martensite is an indication that the metal has cooled so quickly through its critical range that it is hardened or at least partially so as explained in Chapter XVI. If the metal is needed in an annealed condition it should then be reheated as explained in the foregoing pages to slightly below its critical range in order that the troostite and martensite may be converted into sorbite (a tempering process as explained in Chapter XVII).

Structure vs. Heat Treatment. — Some of the many different structures produced by various treatments are shown in a convenient form in Figures 250 and 251 in the case of steels containing respectively 0.30 and 0.50 per cent carbon and otherwise of good commercial quality. The treatments corresponding to each structure are indicated in the accompanying legends.

Spheroidizing of Cementite. — It is now well understood that on slow cooling through the critical range austenite of eutectoid composition is converted into well-defined pearlite made up of distinct parallel plates or lamellæ alternately of ferrite and cementite, while in hyper-eutectoid steel the excess cementite tends to form at the boundaries of the pearlite grains and between the cleavage planes of the austenite. This condition of the cementite of pearlite as well as of the free cementite is not, however, final, not being structurally stable, for if the steel be kept for a sufficiently long time at a temperature but slightly below its critical range, preferably between 600 and 700 deg. C. the cementite shows a marked tendency to collect in the form of rounded particles embedded in a matrix of ferrite. The phenomenon has been called "spheroidizing" by Howe, or when restricted to the pearlite-cementite, "divorcing," on the ground that it constitutes a true divorce between the constituents of pearlite, namely ferrite and cementite. Pearlite that has undergone spheroidizing is sometimes called "granular" or "globular" pearlite.

Both hypo- and hyper-eutectoid steels are reported to spheroidize more readily than eutectoid steel, the free ferrite or cementite probably acting as nuclei. Even eutectoid steel, however, can be completely spheroidized if the heating be continued long enough. Howe states that the transformation is more rapid in a 0.21 per cent carbon than in a 0.59 per cent carbon steel. It seems probable that sorbite yields to the spheroidizing treatment more readily than true pearlite from which it follows that for the purpose of spheroidizing the steel should first be made sorbitic. This can be done by relatively quick cooling through the critical range or as later explained (Chapter XVI) by very quick cooling through the range, thereby producing martensite or troostite, followed by reheating slightly below the critical range which is also the temperature at which the spheroidizing operation should be conducted.

Howe and Levy state that both high heating and long heating above the range

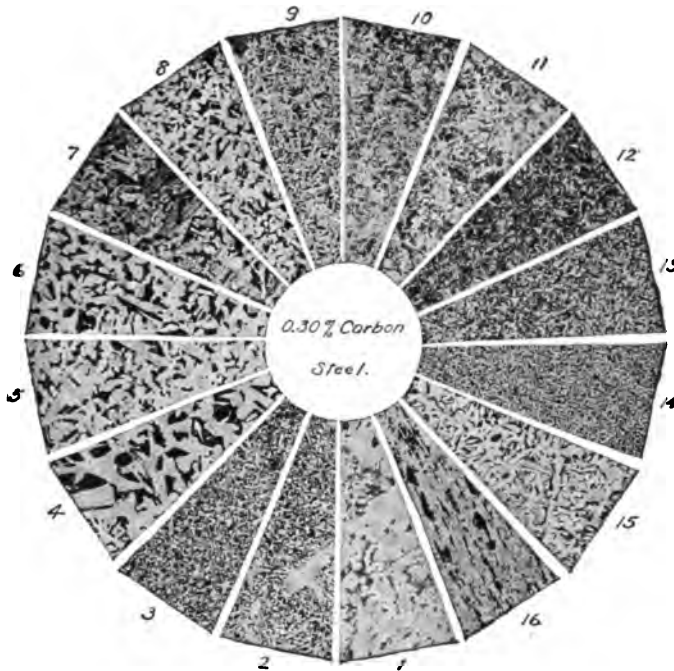


Fig. 250. — Various structures of steel containing 0.30 per cent carbon. Magnified about 30 diameters.

LEGENDA FOR FIGURE 250

1. Cast condition.
2. Cast and improperly annealed.
3. Cast and properly annealed.
4. 1½-in. rolled bar heated for 2 hours at 1000 deg. C. and cooled in furnace.
5. ½-in. rolled bar heated to 1000 deg. C., cooled in furnace.
6. 1½-in. round rolled bar heated to 1000 deg. C. and cooled in furnace.
7. ½-in. round rolled bar heated to 1000 deg. C. and cooled in furnace.
8. ½-in. round rolled bar heated to 900 deg. C. and cooled in furnace.
9. ½-in. round rolled bar heated to 900 deg. C. and cooled in air.
10. ½-in. round rolled bar heated to 900 deg. C. and cooled in oil.
11. ½-in. round rolled bar heated to 900 deg. C. and cooled in water.
12. ½-in. round rolled bar heated to 900 deg. C. and cooled in oil; reheated to 650 deg. C. and cooled in oil.
13. 1½-in. round rolled bar heated to 900 deg. C. and cooled in oil; reheated to 650 deg. C. and cooled in oil.
14. ½-in. round rolled bar finished at proper temperature.
15. 1½-in. round rolled bar finished at high temperature.
16. Cold worked.

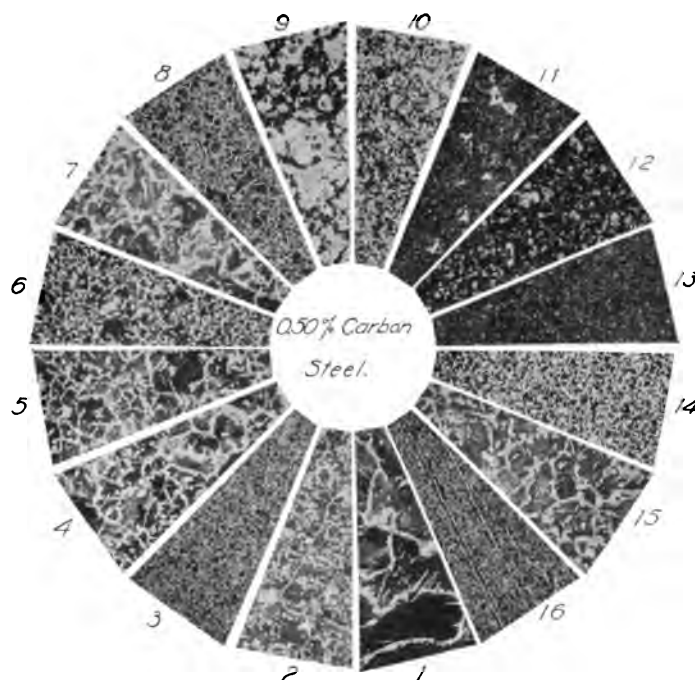


Fig. 251. — Various structures of steel containing 0.50 per cent carbon. Magnified about 30 diameters.

LEGENDA FOR FIGURE 251

1. Cast steel.
2. Cast steel improperly annealed.
3. Cast steel properly annealed.
4. $\frac{1}{2}$ -in. round rolled steel cooled from 1100 deg. C. in the furnace.
5. $\frac{1}{2}$ -in. round rolled steel cooled from 1000 deg. C. in the furnace.
6. $\frac{1}{2}$ -in. round rolled steel cooled from 900 deg. C. in the furnace.
7. $\frac{1}{2}$ -in. round rolled steel soaked 2 hours at 900 deg. C. and cooled in the furnace.
8. $\frac{1}{2}$ -in. round rolled steel cooled from 900 deg. C. in the air.
9. $\frac{1}{2}$ -in. round rolled steel cooled from 1000 deg. C. in water.
10. $\frac{1}{2}$ -in. round rolled steel cooled from 900 deg. C. in water.
11. $\frac{1}{2}$ -in. round rolled steel cooled from 900 deg. C. in oil.
12. $\frac{1}{2}$ -in. round rolled steel quenched in water while passing through critical range.
13. $\frac{1}{2}$ -in. round rolled steel quenched in oil from 850 deg. C.; reheated to 600 deg. C. and quenched in oil.
14. $\frac{1}{2}$ -in. round steel finished at proper temperature.
15. Large forging showing finishing at too high a temperature.
16. Cold worked.

retard the divorcing of pearlite. According to Belaiew the patterns of Damascus steel and its remarkable physical properties are probably caused by a divorcing of ferrite and cementite in macroscopically visible masses produced by prolonged exposure to

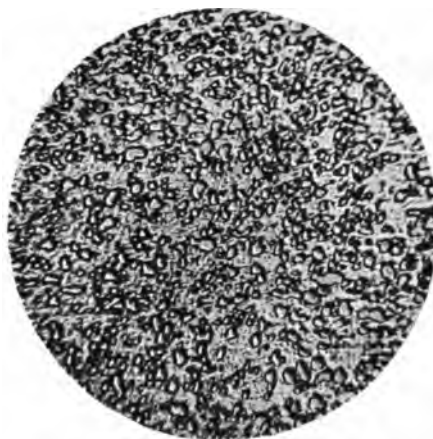


Fig. 252. — Steel. Carbon 0.85 per cent. Magnified 1000 diameters. Spheroidized cementite. (E. H. Peirce.)

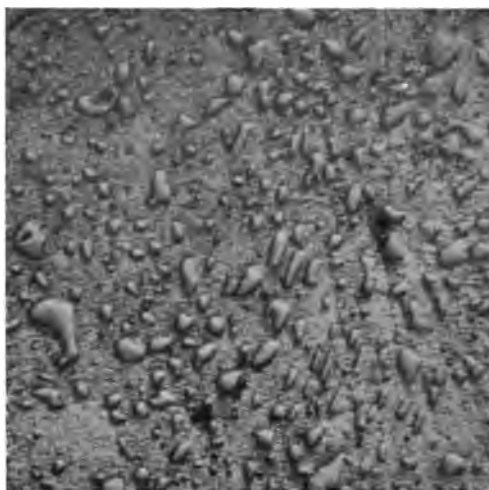


Fig. 253. — Steel. Carbon 1.10 per cent. Magnified 1000 diameters. Spheroidized cementite. (W. J. Burger, Correspondence student.)



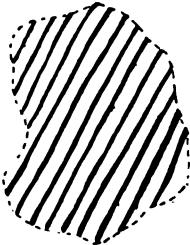



Fig. 254. — Steel. Carbon 1.24 per cent. Magnified 1000 diameters. Spheroidized cementite. (Osmond.)

a temperature not exceeding redness. The spheroidizing treatment greatly decreases the strength and elastic limit, while increasing the ductility and softness and also the resistance to wear (Abbott), these effects being more marked in high than in low carbon steels.

Steel in the spheroidized condition is shown in Figures 252 to 254.

*Showing the Properties of Pearlite and its Decomposition Product.
Fe₃C represented Black.*

Mechanical Properties of Mass.	Microstructure.	Segregation Stages.
Maximum tensile stress about 70 tons per square inch. Elongation on 2 inches=about 10 per cent.		1ST PHASE. "Sorbitic" pearlite with emulsified Fe ₃ C. Very dark on etching.
Maximum tensile stress about 55 tons per square inch. Elongation on 2 inches=about 15 per cent.		2ND PHASE. Normal pearlite with semi-segregated Fe ₃ C. Dark on etching.
Maximum tensile stress about 35 tons per square inch. Elongation on 2 inches=about 5 per cent.		3RD PHASE. Laminated pearlite with completely segregated Fe ₃ C. Exhibiting a play of gorgeous colours when lightly etched.
Maximum tensile stress about 30 tons per square inch.		4TH PHASE. Laminated pearlite passing into massive Fe ₃ C and ferrite.

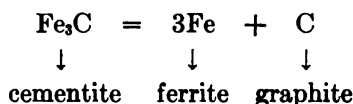
NOTE.—It is important to remember that in a single section of steel two or even all three phases of pearlite may be observed in juxtaposition gradually merging into each other.

Fig. 255. — (Arnold.)

Varieties of Pearlite. — From the foregoing it will be evident that several varieties of pearlite are to be considered and that the physical properties of steel will depend greatly upon the character of the pearlite it contains. Arnold considers four varieties of pearlite which are well illustrated in Figure 255. His first phase, which he calls "sorbitic" pearlite, is generally called sorbite by other writers. The character and physical properties of sorbite have been described, as well as some of the conditions necessary to its formation. His second and third phases, to which he gives the names respectively of "normal" and "laminated" pearlite, are both true pearlite, the thicker lamellæ of the latter being due to a slower cooling through the critical range. His fourth phase is pearlite in the process of spheroidizing.

It is now understood that true, i.e. clearly laminated, pearlite only has a constant composition, being in this respect similar to all eutectic and eutectoid alloys as explained in Chapter XXV. In hypo-eutectoid steel sorbite generally contains more ferrite and, therefore, a smaller percentage of carbon than pearlite, while in hyper-eutectoid steel it generally contains more cementite, hence a larger percentage of carbon. Moreover, while in true pearlite the carbon is probably wholly present as crystallized Fe_3C (cement carbon), in sorbite a part of it remains dissolved (hardening carbon) and it is probably to the presence of carbon in solution that sorbite owes its greater strength and its decreased ductility.

Graphitizing of Cementite. — It will be explained in another chapter that the carbide Fe_3C (cementite) is not the most stable form that can be assumed by carbon when alloyed with iron. It will be shown that cementite tends to break up into iron and graphite according to the reaction



and that the graphite form is the final stable condition of carbon. This graphitizing tendency of cementite remains latent unless the conditions be favorable to its activity. These conditions are (1) long exposure to a temperature exceeding the critical range and slow cooling, (2) the presence of much carbon, and (3) the presence of silicon or of some other elements exerting a similar influence. It will be shown that this tendency of cementite to be converted into graphite and iron is responsible for the production of so-called malleable castings and, probably, also for the production of gray cast iron. In the case of steel, because of the relatively small amount of carbon present (not exceeding 1.75 or at the most 2 per cent), the graphitizing tendency is slight. Long exposure of hyper-eutectoid steel, especially if it contains more than one per cent carbon, however, to a temperature exceeding its critical range, is always likely to produce a small amount at least of graphitic carbon greatly impairing thereby, if not ruining, the metal. An instance of graphite formation in high carbon steel is shown in Figures 256 and 257. There is little doubt but the free cementite present in hyper-eutectoid steel, and formed as the steel cools from its $A_{r_{cm}}$ to its $A_{r_{3.2.1}}$ point, is more readily converted into graphite than the cementite included in the pearlite. Once the graphitizing is started, however, it may be carried to completion and include the whole of the cementite present. This indeed is what happens in certain grades of malleable cast iron and of gray cast iron which contain practically the totality of their carbon in the form of graphite. The presence of some free cement-

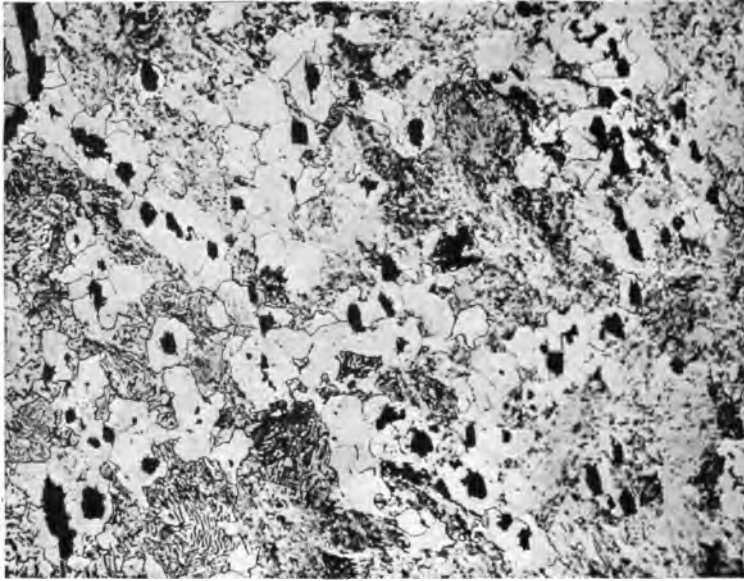


Fig. 256. — Steel. Carbon 1.25 per cent. Magnified 150 diameters. Annealed five hours at 830 deg. C. (C. C. Buck, Correspondence Course student.)

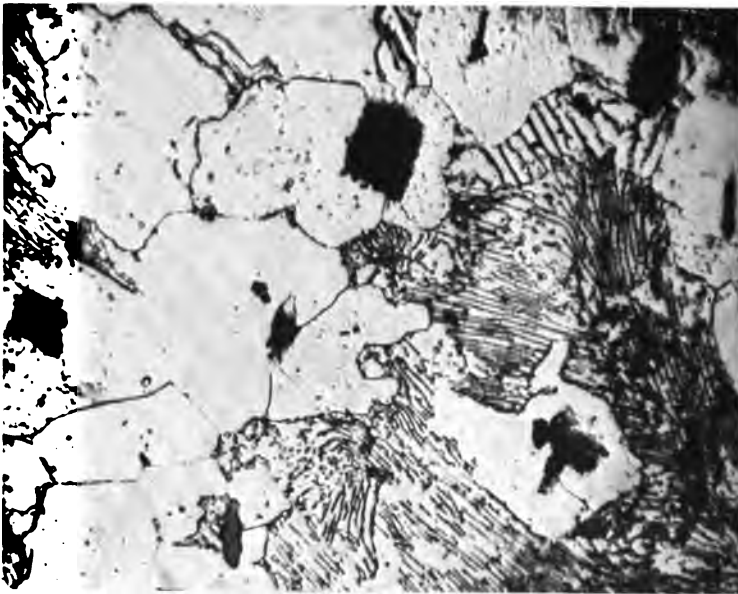


Fig. 257. — Steel. Carbon 1.25 per cent. Magnified 670 diameters. Annealed five hours at 830 deg. C. (C. C. Buck, Correspondence Course student.)

ite appears to be necessary to start the graphitizing, which would explain why it does not take place in hypo-eutectoid steel. The author at least never had a case of graphite formation in such steels brought to his attention nor was he ever able to produce graphite in hypo-eutectoid steel.

Over Heating. — Long exposure of steel to a high temperature necessarily develops a very coarse structure and the metal is then said to have been overheated. Stead describes the coarse crystalline structure of overheated steel containing from 0.20 to 0.50 per cent carbon as triangular arrangements of ferrite and pearlite, and that of steel containing from 0.50 to 0.70 per cent carbon as large ferrite cell walls and offshoots of ferrite penetrating the pearlite (Fig. 258). Overheating should not be confounded with burning; overheated steel can be readily restored to a normal

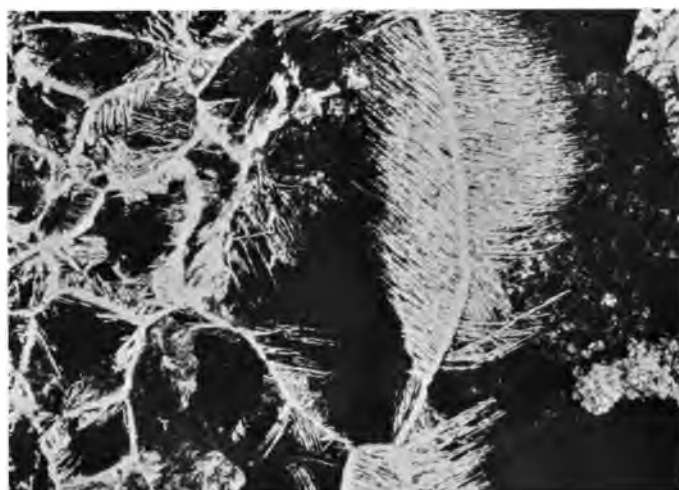


Fig. 258. — Steel. Carbon about 0.50 per cent. Heated to about 1100 deg. C. (P. J. Neely, Correspondence Course student.)

condition by merely heating above the critical range, and is neither red short nor cold short, while burnt steel is extremely brittle.

Burnt Steel. — When high carbon steel is heated to a temperature approaching its melting-point, it becomes extremely red short as well as cold short while its fracture becomes very coarse and shiny. The steel in such condition is said to be burnt. It was generally believed that the red shortness of burnt steel could not be cured short of remelting, but Stead now insists that if burnt steel be allowed to cool completely and is then reheated to a proper temperature it can be rolled and forged as well as if it had not been burnt. It is held by some that the burning of steel is due to the evolution of gases under the influence of a high temperature, chiefly carbon monoxide, resulting from atmospheric oxygen finding its way through the pores of the metal and combining with some of the carbon, although according to Howe other occluded gases, such as hydrogen and nitrogen, may also contribute. These gases force the crystalline grains apart, destroying their cohesion, hence the brittleness of the metal. Oxidized membranes are also frequently found surrounding some of the

grains, their presence readily explaining the impossibility of restoring burnt steel by forging since they would prevent the welding of adjacent grains. Instances of the structure of burnt steel are shown in Figures 259 and 260. Howe defines burning as being "a mechanical separation of the grains on extreme overheating." Some writers have argued, apparently on good ground, that burning will not take place unless the steel has been heated to so high a temperature that it has actually begun to melt, the explanation being perfectly consistent with the well-known fact that high carbon steel burns much more readily than low carbon steel. To make the matter clear, let us consider the diagram of Figure 261 in which the solidification period of steel is shown as influenced by its carbon content. This diagram will be discussed at greater length in another chapter. Let us for the present note (1) that as the carbon increases from 0 to 2.0 per cent the solidification of the steel is lowered from *A* to *B*, that is



Fig. 259. — Burnt steel. Carbon 1.24 per cent. Magnified 20 diameters. Quenched at a white heat. Unetched. (Osmond.)



Fig. 260. — Burnt steel. Magnified 30 diameters. (Stead.)

from 1500 deg. C. to 1325 deg., (2) that while carbonless iron solidifies at a constant temperature, namely 1500 deg., as the carbon increases, the range of temperature covered by the solidification period increases likewise, extending from *B* to *C* with 2 per cent carbon, that is from 1325 to 1130 deg. C. *ABC* then represents the solidification zone of steels of increasing carbon content and the heating of the metal to any point within this zone, when it is partly melted, will cause it to burn. It follows from this that carbonless iron and very low carbon steel can be heated to a very high temperature without burning, while the danger of burning increases with the carbon. With 0.50 per cent carbon, for instance, the burning zone extends from 1400 to 1450 deg., with 1.0 per cent it extends from 1310 to 1400 deg., with 1.50 per cent carbon from 1210 to 1360 deg. In short, as the carbon increases the steel burns more readily (1) because its melting-point is lowered and (2) because its solidification zone, which is also its burning zone, is widened. According to the theory it should not be possible to burn carbonless iron, and indeed the author does not know that the claim has ever been made that carbonless iron could be burnt.

If *ABC* represents a burning zone into which steel cannot be brought without having its useful qualities destroyed, we naturally ask why all steels are not so injured seeing that they must pass at least once through this zone in cooling from the molten condition. The reason why steel does not burn on solidifying and further cooling is explained by Howe on the ground that while steel ingots or other castings solidify, much hydrogen is given out which may mechanically restrain the oxygen from entering and also counteract it, preventing thereby the evolution of CO from within and the formation of oxidized films, the chief causes of burning. It is also possible, Howe says, that the greater kneading which an ingot undergoes cures burn-

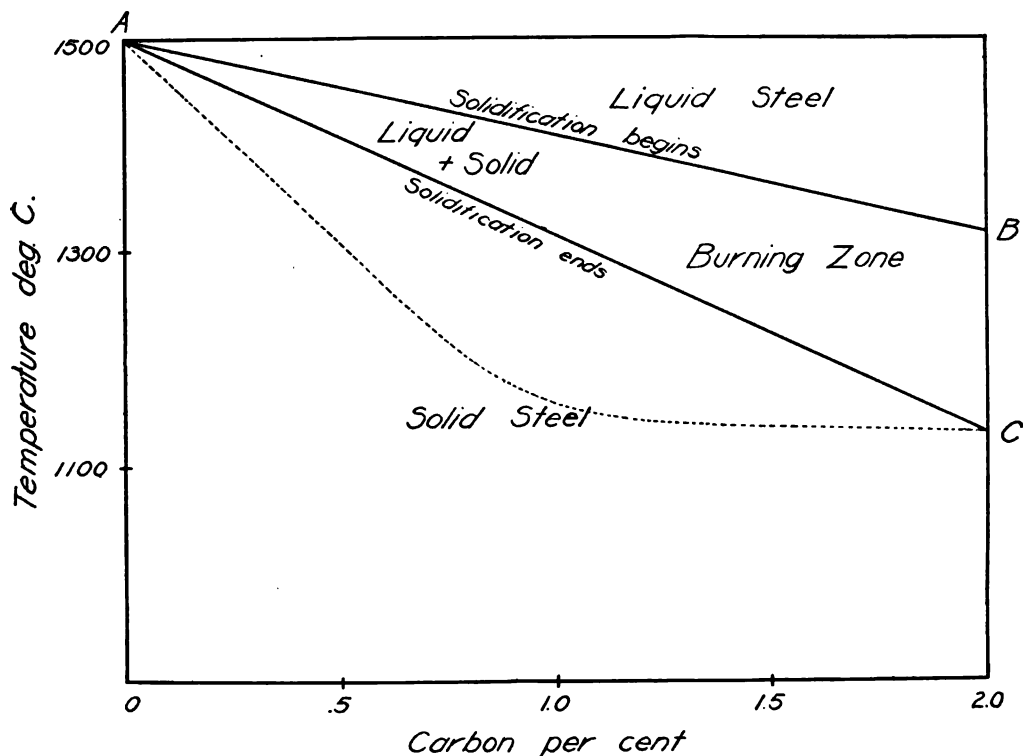


Fig. 261. — Diagram depicting the burning temperature range.

ing, while the slight kneading possible in reworking a steel bar does not. This, however, would not explain why steel castings, which undergo no work at all, are not burnt, unless it is because they are generally protected from atmospheric oxidation by their molds (Howe).

Burning should not be confounded with overheating. Overheated steel has a very coarse structure and fracture, but it can be restored by heat treatment alone, or at least by heating and forging, while burnt steel is believed by many to be incurable. Overheating results from heating close to but below *AC* (Fig. 261), generally for a considerable length of time, while, as explained, the temperature in burning is carried above *AC*.

Important results recently obtained by Gutowsky would place the end of the

solidification of various carbon steels as indicated by the dotted line in Figure 261. If these are the correct temperatures at which solidification is complete, it follows that the burning zone is wider than was generally believed before the publication of these results.

Stead rejecting the oxidizing gases theory believes that the burning of steel resulting from heating the metal to incipient fusion, causes the formation of globules or envelopes rich in phosphorus (hence fusible) round the crystals and that their presence or absence is a proof of the steel having been burnt or not. When they occur they are readily detected by etching the metal with his cupric reagent (Chapter II).

The burnt steel in Fig. 262 has been etched with this reagent. The white net-

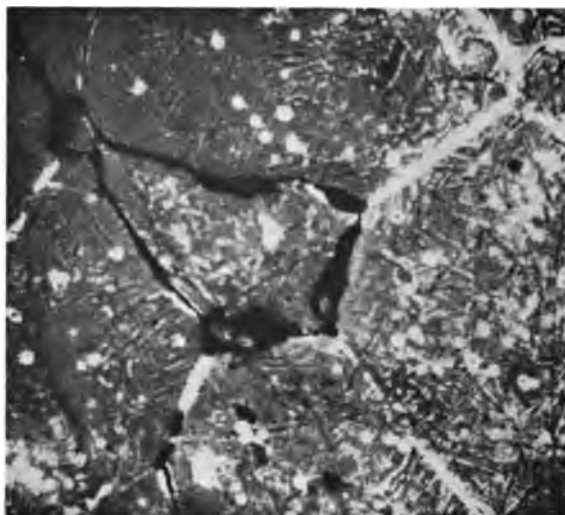


Fig. 262. — Burnt steel etched with Stead's cupric reagent showing globules and envelopes rich in phosphorus. Magnified 50 diameters. (Stead.)

work and white particles show the segregation of portions rich in phosphorus. Stead writes:

"The question is often asked of the expert, when steel samples have broken up at the rolls, whether the material is naturally red short or has been burnt. The sides of cracks found in the steel, whether simply red short or burnt, are always lined with oxide; and the expert, in conducting his examination, must be careful to select portions free from cracks and to polish and etch them. If they be free from globular specks rich in phosphorus, it may be concluded that the material has not been burnt and is naturally red short, but if such specks be present the reverse conclusion will be justified."

Crystalline Growth of Austenite Above the Critical Range. — Above its critical range steel is composed of polyhedral crystalline grains of austenite, which are made up of small crystals (probably octahedra) similarly oriented in the same grain but whose orientation changes from one grain to the next. Indeed it is this lack of uniformity of the orientation of the crystalline matter building up the grains that gives

existence to these grains, for if all the small crystals of which they are composed were similarly oriented, clearly there would be but a single allotriomorphic crystal or grain. If steel be maintained for a long time above its critical range, the austenite grains of which it is composed show a tendency to grow in size through adjoining grains assuming like crystalline orientation and, therefore, merging into a single and correspondingly larger grain. This growth increases with the temperature and with the duration of the treatment. Given a sufficiently long time and sufficiently high temperature, but one grain must be formed. This, as already seen in Chapter XIII, is actually what takes place in meteorites during the cooling of which the prevailing conditions are such as to produce this uniformity of orientation. It follows from the above considerations that on annealing, if the metal be kept a long time above its critical range, even but slightly above it, a coarser austenite will be formed which in turn implies, after slow cooling, a coarser pearlitic or sorbitic structure. In hypo-eutectoid steel the grains of austenite will expel some free ferrite, and in hyper-eutectoid steel some free cementite, before being converted into pearlite, but the final pearlite grains will nevertheless increase in size with the size of the original austenite grains. The structure of steel containing 0.50 per cent carbon kept two hours at 1150 deg. C. and cooled in air has been shown in Figure 228. The very large sorbitic grains formed prove the existence above the range of equally large, or even larger, austenitic grains. The cooling through the range was so rapid that but a small amount of free ferrite was separated, the sorbite grains, therefore, representing nearly the exact size of the austenite grains.

In Figure 263 an attempt has been made to depict this relation between the austenitic structure above the range and the corresponding pearlitic or sorbitic structure below the range. The steel considered is supposed to be hypo-eutectoid and to contain, after slow cooling, a large proportion of free ferrite. *A* is intended to represent a piece of this steel made up of nine relatively small austenitic grains formed on short exposure above the range. On cooling through the range ferrite is liberated and the residual austenite grains converted into as many pearlite grains as shown in *A'*. The small squares of the matrix surrounding the pearlite grains represent as many small ferrite grains. After a longer exposure, possibly at a higher temperature, the steel will be made up of larger austenite grains, say of four grains as shown in *B*, and these, on slow cooling through the range, will be converted after rejection of ferrite into four pearlite grains as indicated in *B'*. Theoretically, at least, we may assume that the temperature above the range may be so high and the exposure at that temperature so long that but a single austenite grain is formed, the entire mass having assumed a uniform crystalline orientation as shown in *C*. On slow cooling a single pearlite grain would then be formed surrounded by free ferrite in the form of small grains as depicted in *C'*. An exceedingly slow cooling through and below the range would have a tendency to cause the free ferrite to crystallize into larger grains and eventually to form but a single grain as indicated in *C''*.¹ Finally, as will be later explained, on very long exposure to a high temperature the cementite should, theoretically at least, be converted into as many graphite particles as there are austenite grains and, therefore, into a single graphite particle in case there is but a single grain of austenite, the steel then consisting, after slow cooling, of a kernel of graphite surrounded by uniformly oriented ferrite as shown in *C'''*. As already explained, how-

¹ Such slow cooling, as previously explained, would also have a tendency to cause the spheroidizing of cementite.

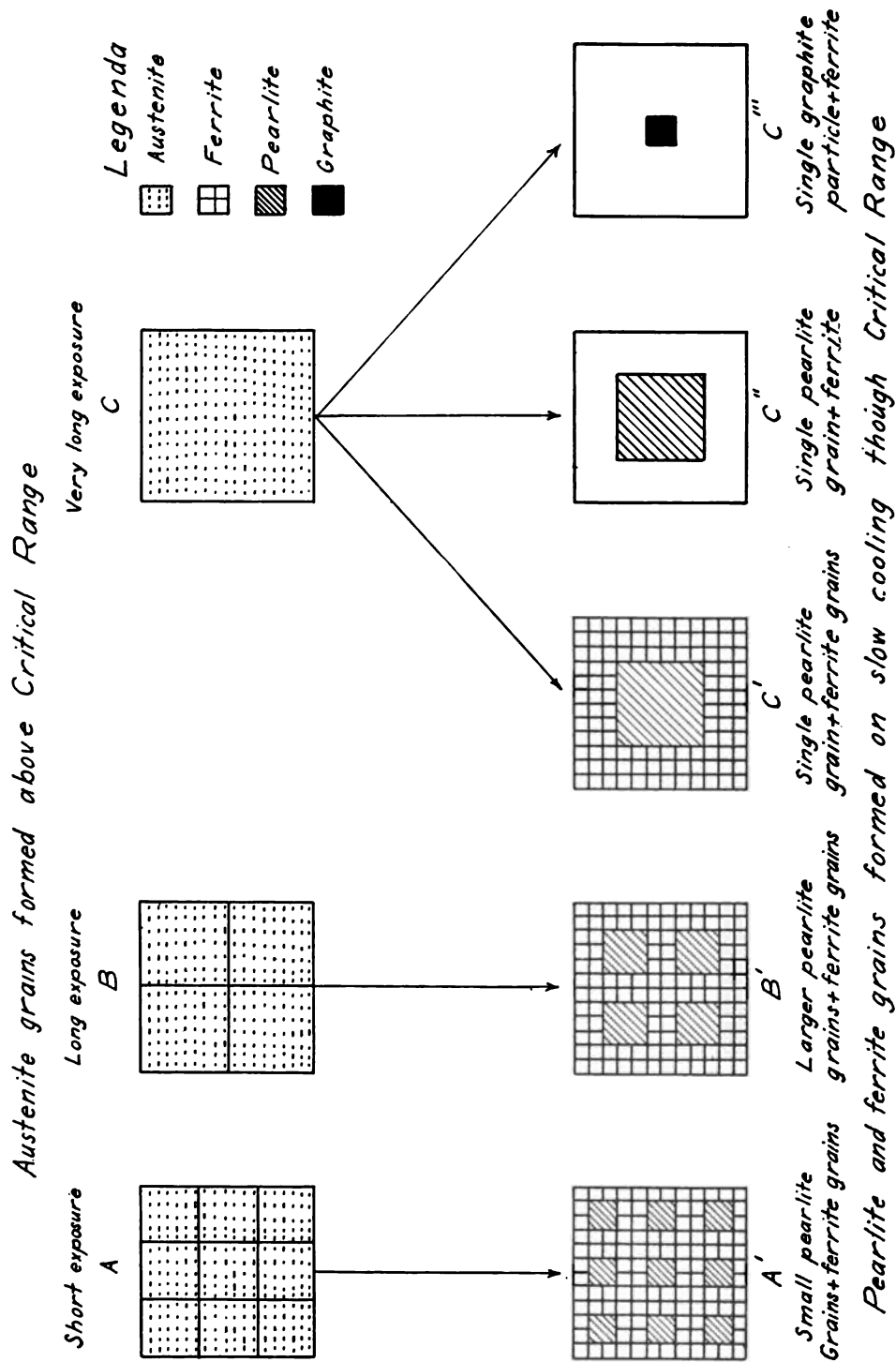


Fig. 263.

ever, this breaking up of cementite into graphite and ferrite does not take place unless a considerable amount of carbon is present, namely over 1 per cent.

The conditions depicted in A' , B' , C' , C'' , and C''' are conditions of equilibrium, according to the phase rule, since but two phases are present. It is now believed, however, that A' , B' , C' , and C'' represent metastable equilibrium while C''' , only, represents stable equilibrium. The phase rule will be considered in another chapter when these remarks will be made clear.

Crystalline Growth of Ferrite Below the Critical Range. — Stead in 1898 showed that *strained* ferrite, when heated close to but below the critical range of the metal, undergoes a marked crystalline growth caused by adjoining ferrite grains assuming the same crystalline orientation and therefore merging into a larger grain. It seemed evident from Stead's experiments that unless the ferrite be strained (through cold



Fig. 264. — Steel. Carbon 0.05 per cent. Magnified 6 diameters. Subjected to Brinell ball test under pressure of 6000 kilograms and heated to 650 deg. C. for seven hours. Vertical section through bottom of spherical depression. (J. O. Connolly in the author's laboratory.)

working or otherwise) it will not grow on annealing, and also that the presence of a relatively small amount of carbon (some 0.15 per cent or more) effectively prevents the growth of the ferrite grains, apparently because of the pearlite particles standing in their way and preventing their merging. The author recently conducted in his laboratory some experiments, the results of which throw additional light upon this crystalline growth.¹

The following extracts from a paper by the author presented at the sixth Congress of the International Association for Testing Materials describe briefly some of the most significant results obtained.

In Figure 264 is shown the slightly magnified structure of a steel containing 0.05 per cent carbon which had been subjected to the Brinell ball test² under a pressure of

¹ These experiments were made by J. O. Connolly, at the time a research student at Harvard University, now with the American Steel and Wire Co.

² In using the Brinell ball test as a suitable means of straining ferrite in order to study its growth on annealing the author followed Charpy.

Austenite grains formed above Critical Range

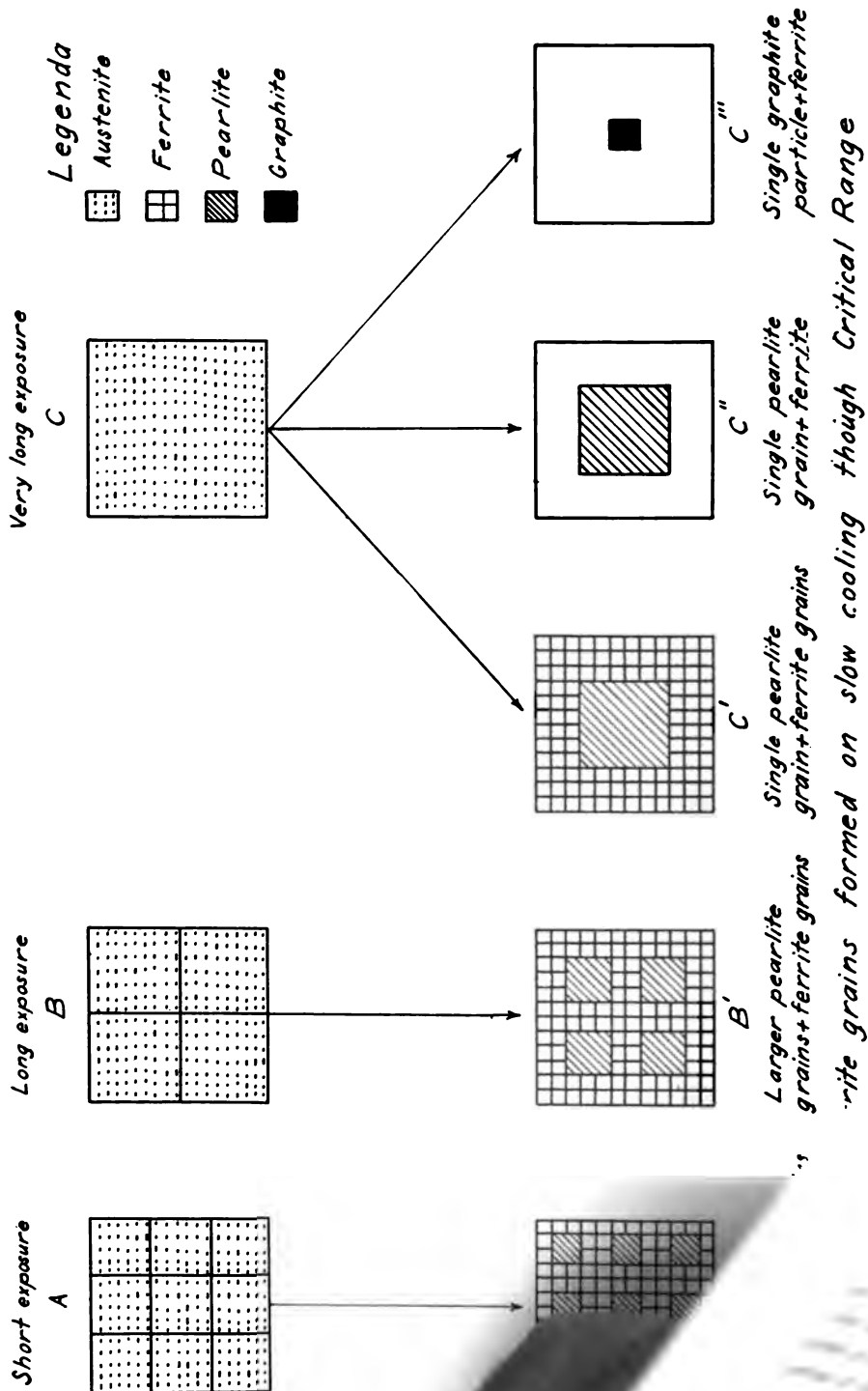


Fig. 263.

ever, this breaking up of cementite into graphite and ferrite does not take place unless a considerable amount of carbon is present.

The conditions depicted in A' , B' , C' , C'' , and D' represent stable equilibrium, according to the phase rule, since but two phases are present. It is believed, however, that A' , B' , C' , and C'' represent metastable equilibrium, and only, represents stable equilibrium. The phase rule will be discussed in a later chapter when these remarks will be made clear.

Crystalline Growth of Ferrite Below the Critical Range — It has been found that *strained* ferrite, when heated close to but below the critical range, undergoes a marked crystalline growth caused by an increase in the same crystalline orientation and therefore *preferred* growth. This is evident from Stead's experiments that unless the ferrite is strained



Fig. 264. — Steel. Carbon 0.05 per cent. Brinell ball test under pressure of 6000 pounds for seven hours. Vertical section through Connolly in the author's laboratory.

Magnified
all test under
ted to 650 deg.
section through
(J. O. Connolly in

working or otherwise) it will not grow. A relatively small amount of carbon, however, the growth of the ferrite grains, as shown in their way and preventing the same. In laboratory some experiments, the result is crystalline growth.¹

The following extracts from a paper presented at the progress of the International Association of Metallurgists, the most significant results being:

In Figure 264

It will be obvious that the upper part of the bar was subjected to severe tension and the lower part to severe compression. Between the upper and lower parts a neutral zone existed, neither to tension nor to compression, and in the center of the bar no growth took place, the metal became gradually more severely strained. As soon as the critically strained portion was reached, the growth of maximum intensity, and (3) this growth decreased as the metal became more severely strained, being very slight if existing at its maximum, that is, near the upper and lower parts of the bar, free from growth as the distance from the

6000 kilograms and then annealed at 650 deg. C. for seven hours. The section shown is a vertical one passing through the bottom of the spherical depression made by the 10-mm. ball used. It will be obvious that the strain was most severe at *A*, that is at the very bottom of the depression, and that it decreased gradually in intensity from *A* to *D*. The following features of the structure should be noted as having special significance: (1) At *D* where the metal was but slightly if at all strained no crystalline growth occurred, (2) at *C* where the strain must have been more severe a sudden growth of maximum intensity has taken place, (3) from *C* to *B* as the severity of the strain increases the crystalline growth shows a gradual *decrease*, and (4) from *B* to *A*, that is with further increase of the intensity of the strain, no crystalline growth has taken place. These observations point to the conclusion that ferrite

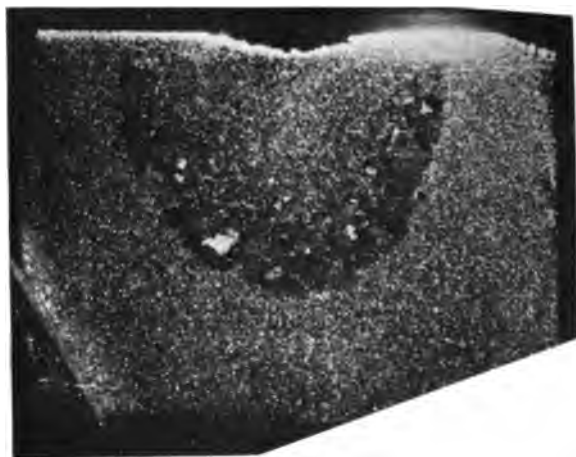


Fig. 265. — Steel. Carbon 0.05 per cent. Magnified 6 diameters. Subjected to Brinell ball test under pressure of 3000 kilograms and heated to 650 deg. C. for seven hours. Vertical section through bottom of spherical depression. (J. O. Connolly in the author's laboratory.)

grains will not grow on annealing below the critical range unless they have been subjected to a certain stress creating a certain strain, and that they will not grow if that stress, and therefore the resulting strain, has been exceeded. In other words, they point to the existence of a critical strain producing growth, strains of greater or less magnitude being ineffective. The narrow region occupied by the critically strained metal should also be noted as well as the very sharp line of demarcation between the critically strained and the under-strained metal. The separation of the critically strained metal from the over-strained is not so sharp.

Similar experiments were repeated many times and like results always obtained.

A piece of the same steel was subjected to exactly the same treatment, except that the ball pressure applied was 3000 kilograms or half the pressure applied to the previous one. The crystalline growth resulting from the annealing of this sample is shown in Figure 265. Because of the smaller stress applied, the critically strained portion of the metal is nearer the depression. This would naturally be expected.

Here, as in the previous case, we have three distinct regions: (1) the metal surrounding the depression and extending to a certain distance which was too severely strained to grow, (2) the critically strained metal in the form of a spherical shell, and (3) the rest of the metal unstrained or too feebly strained for the growth to take place. Figure 266 is a section through a similar sample, the specimen having been ground level with the bottom of the depression. The occurrence in this section of a ring showing crystalline growth will be readily understood.

In Figure 267 is shown the structure of a bar of the same steel which after having been completely bent was subjected to annealing (seven hours at 650 deg. C.). A piece of the bent portion of this bar was then cut and a longitudinal section through

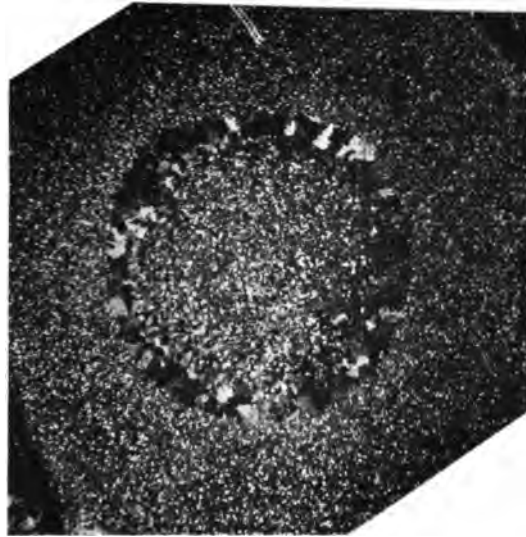


Fig. 266. — Steel. Carbon 0.05 per cent. Magnified 6 diameters. Subjected to Brinell ball test under pressure of 3000 kilograms and heated to 650 deg. C. for seven hours. Horizontal section through bottom of spherical depression. (J. O. Connolly in the author's laboratory.)

its center prepared for microscopical examination. It will be obvious that the upper part of the bent portion of the bar was subjected to severe tension and the under part to severe compression. Somewhere between the upper and lower parts a neutral plane existed which was subjected neither to tension nor to compression, and in the vicinity of this plane the metal was but slightly strained. Moving in both directions from this neutral plane, the metal becomes gradually more severely strained. Figure 267 shows that (1) in the center of the bar no growth took place, the metal being here under-strained, (2) as soon as the critically strained portion was reached a very abrupt growth occurred of maximum intensity, and (3) this growth decreased gradually as the metal became more severely strained, being very slight if existing at all where the strain was maximum, that is, near the upper and under parts of the bend. The widening of the central zone, free from growth as the distance from the

bend increases, is also consistent with the existence of a critical strain, for it is evident that the portion of unstrained or under-strained metal increases with that distance. Incidentally this experiment shows that tension is apparently as effective as compression in producing crystalline growth, there being apparently no difference in the size of the ferrite grains between the upper and under parts of the bar. The critically strained portions occupy also nearly the same position with regard to the outside surfaces, that is, they occur at the same depth. Their width also appears to be the same.

Bars of the same steel were subjected to compression, shearing, and twisting stresses and the results obtained were in every case consistent with the existence of a critical strain.

With a view of securing some data in regard to the magnitude of the critical stress needed to induce growth on annealing, a number of bars of the same steel were sub-

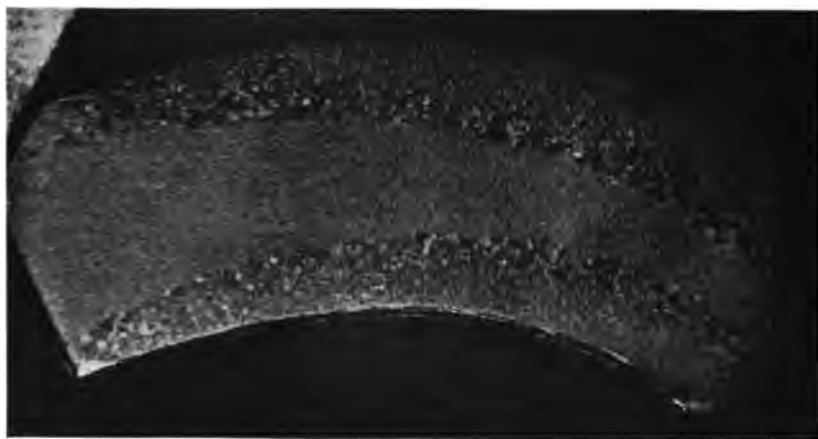


Fig. 267. — Steel. Carbon 0.05 per cent. Magnified 3 diameters. Bar bent double and heated to 650 deg. C. for seven hours. Longitudinal section through center of bent portion. (J. O. Connolly in the author's laboratory.)

jected to tensile stresses of increasing intensity, annealed at 650 deg. seven hours, and in every case a cross section of the strained and annealed bar was prepared for microscopical examination. The elastic limit or rather yield point of the metals was in the vicinity of 28,000 lbs. per square inch, and its ultimate strength 45,600 lbs. per square inch.

In Figures 268 to 271 are shown the structures of the bars subjected respectively to stresses of 38,000, 40,000, 42,000, and 44,000 lbs. per square inch.

These tensile tests afford another conclusive evidence of the existence of a critical strain and the fact that a stress of 40,000 lbs. per square inch produces a marked growth while stresses but slightly inferior or superior, namely, 38,000 and 42,000 lbs. per square inch, do not induce growth is an indication of the narrowness of the range of the critical stress.

A striking illustration of the existence of critically strained metal is shown in Figure 272 after C. Chappell, in the form of longitudinal sections through broken tensile test pieces heated for two hours at 600 deg. C. Here again the demarcation

between the under-strained portion and the critically strained one is sharper than between the latter and the over-strained portion.

The contention of some that if time be given the over-strained portion also will grow does not remove the gap existing between critically strained metal responding

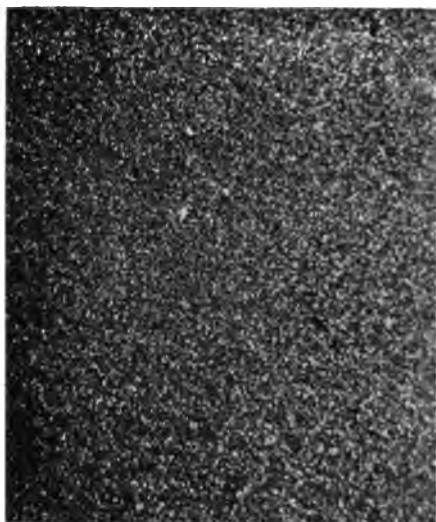


Fig. 268. — Tensile stress, 38,000 lbs. per sq. in.

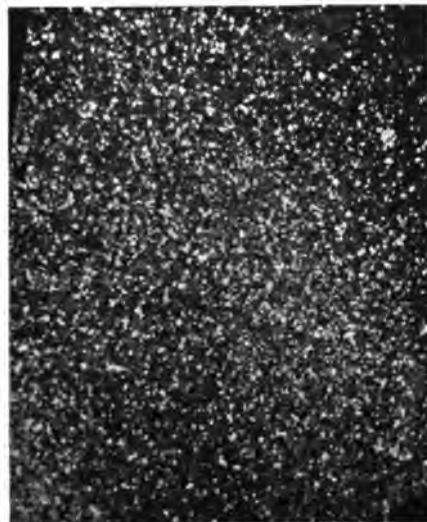


Fig. 270. — Tensile stress, 42,000 lbs. per sq. in.

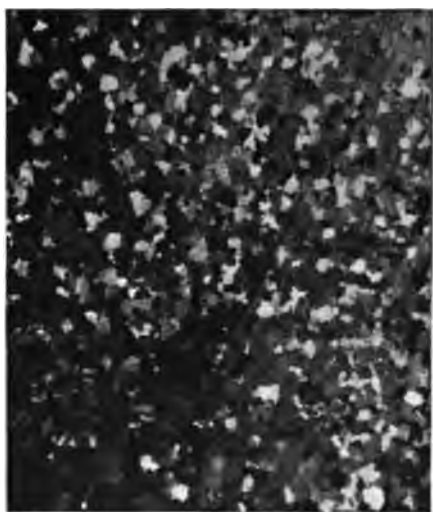


Fig. 269. — Tensile stress, 40,000 lbs. per sq. in.

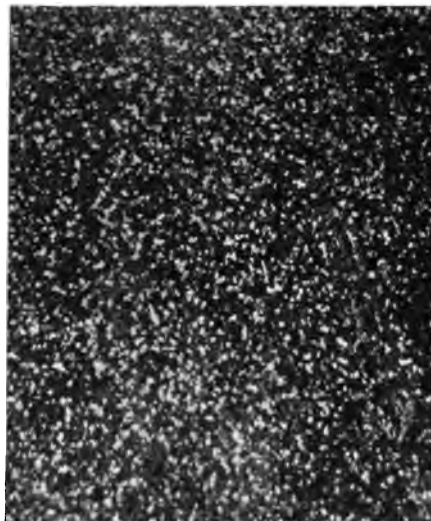


Fig. 271. — Tensile stress, 44,000 lbs. per sq. in.

so readily to the annealing treatment and over-strained metal, if not absolutely recalcitrant, at least extremely refractory to the treatment.

In subjecting electrolytic iron of great purity to the treatments producing the crystalline growth of ferrite described above, Stead reports that he was unable to

cause its grain to grow. The author likewise has never succeeded in producing a growth, at least in any appreciable degree, in wrought iron nor in practically carbonless iron such as American ingot iron. It seems certain that a small amount of carbon, preferably in the vicinity of 0.05 per cent, must be present. On the other hand

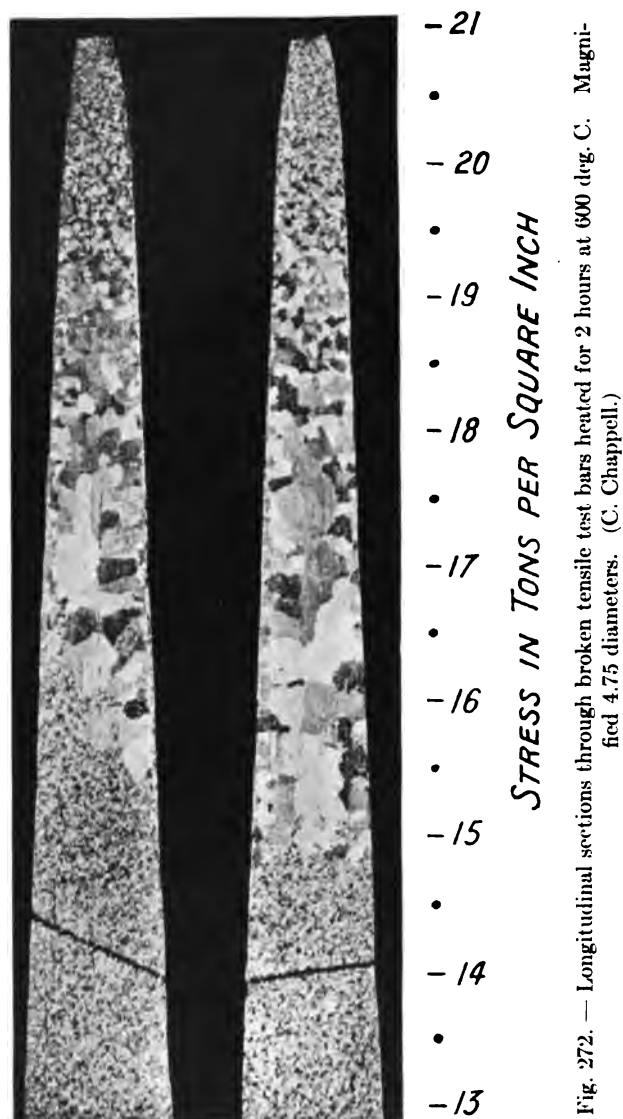


Fig. 272. — Longitudinal sections through broken tensile test bars heated for 2 hours at 600 deg. C. Magnified 4.75 diameters. (C. Chappell.)

he has never succeeded in coarsening appreciably, by similar treatments, the grain of steel containing over 0.12 per cent carbon. It would seem therefore that we must also recognize the existence of a critical carbon content (0.04 to 0.12 per cent) above or below which ferrite grains will not grow on annealing below the range, even if they have been critically strained.

From what has been said of the crystalline growth of strained ferrite under its

critical range, and considering that cold drawn steel wires are frequently annealed at such temperature, it may reasonably be asked why they are not rendered thereby coarsely crystalline and brittle. Obviously because steel wires when subjected to the annealing treatment are generally in a decidedly over-strained condition. If very low carbon steel wire be given a draft so light that it is critically strained, heating it for a sufficient length of time at some 600 deg. C. will cause the crystalline growth of ferrite as should be expected. In such critically strained metal, however, the growth may be prevented by heating to a decidedly lower temperature, as for instance to 525 or 550 deg. C., which is sufficient to remove materially the brittleness resulting from cold working or, of course, by annealing above the critical range.

According to Kenneth B. Lewis, in wire drawing the reduction should not be less than 20 per cent in order to avoid the production of critically strained metal and hence dangerous crystalline growth on subsequent annealing below the thermal critical range.

Robin believes that the straining of ferrite results in the creation of a number of nuclei (*germes*) from which new grains will grow on annealing. To account for the existence of a critical strain it might be argued (1) that in under-strained metal these nuclei are not formed, (2) that in critically strained metals a few nuclei are produced giving rise on annealing to a few large grains, and (3) that in over-strained metal a great many nuclei form, producing on annealing a great many and therefore, necessarily, smaller grains.

Beilby's amorphous theory briefly explained in Chapter V seems to afford the most acceptable explanation of the crystalline growth of strained ferrite below its critical range, on the ground that the amorphous iron produced by straining, re-crystallizes below the range. Howe has suggested the following ingenious hypothesis to account for the existence of a critical strain: (1) the crystalline growth of ferrite is an electrolytic process in which the amorphous iron acts as electrolyte, (2) if the iron be over-strained the quantity of amorphous iron is so great, that is there is so much electrolyte, that electrolysis can take place across it only very slowly, hence the slowness or entire absence of crystalline growth, (3) in under-strained iron there is no growth because of the presence of an insufficient amount of amorphous iron, that is of electrolyte, and (4) in critically strained metal the proportion of amorphous iron is such as to lead to rapid electrolysis, that is to rapid growth. "In short," Howe writes, "the very rapid coarsening implies the presence of enough electrolyte to give electrolysis a chance, yet not so much electrolyte as to cause too great a barrier to electrolysis by its width. Again, if the quantity of the electrolyte was excessive that would mean that the quantity of crystalline iron remaining was small. Now it is only the crystalline iron which can form grains and hence can coarsen, and if this iron is reduced to too small a quantity it might readily follow that the residual crystalline iron was not abundant enough to form large grains."

Brittleness of Low Carbon Steel. — The crystalline growths and other structural changes described in the foregoing pages lead naturally to the consideration of the brittleness occasionally exhibited by low carbon steel. Since steel containing very little carbon is essentially made up of ferrite, its occasional brittleness must be due to the occasional brittleness of ferrite, a constituent by nature soft and ductile. Stead has indicated two kinds of brittleness from which ferrite may, and occasionally does suffer, namely, (1) "inter-granular" brittleness and (2) "inter-crystalline" or "cleavage" brittleness.

By inter-granular brittleness is meant a lack of cohesion between the ferrite grains leading to ready fracture under shock, the line of fracture following the boundary lines of the grains. Such brittleness is usually due to the presence of impurities forming brittle and more or less continuous membranes surrounding the grains. The presence of much phosphorus, however, appears to produce inter-granular brittleness without producing surrounding membranes.

Inter-crystalline or cleavage brittleness is caused by the ferrite grains assuming *nearly* the same crystalline orientation so that the plane of fracture follows the cleavage planes and passes from grain to grain almost in a straight line. The diagram shown in Figure 273 will make this clear. The cross lines represent the cleavage planes in each grain. In *B* the metal is made up of large ferrite grains but the crystalline orientation of these grains is so heterogeneous that a line of fracture cannot

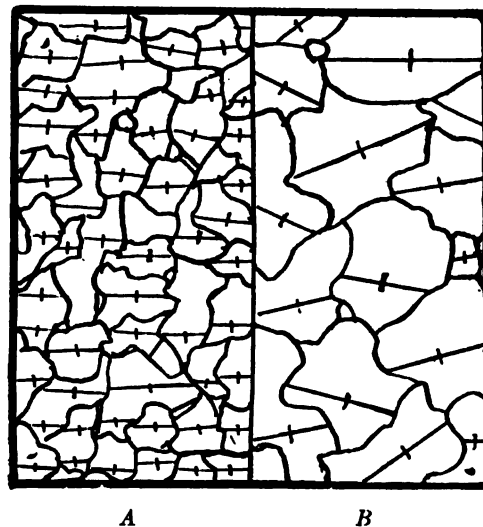


Fig. 273. — (Stead.)

readily be developed and pass from grain to grain, the abrupt change of crystalline orientation encountered at each boundary line acting as an effective obstruction to its advance. In *A*, on the contrary, while the grains are smaller they have nearly the same orientation, hence fracture may proceed from grain to grain with much greater ease and in a nearly straight line. Fortunately, so uniform a crystalline orientation is not often met with and cleavage brittleness is a rather rare occurrence. It can be cured by reheating the steel to 900 deg. or higher.

Stead also noticed that low carbon steel plates rolled below the critical range and, therefore, strained, and annealed likewise below the range, often exhibit a tendency to break in three directions, namely, at 45 deg. to the direction of rolling and at right angles with the surface of the plates, that is, in the directions of the three cleavage planes of a cube having four faces at 45 deg. to the edges, and two faces parallel to the surface of the plates. This he calls "rectangular" brittleness. "We are led from this to conclude," Stead writes, "that, just as light impresses a latent image on a bromide photographic plate which cannot be seen but is developed and made mani-

fest by the action of certain chemical agencies, so the rolling appears to impress a latent disposition in the steel to crystallize in certain fixed positions, and annealing develops it afterwards." The brittleness here referred to is undoubtedly caused by the crystalline growth of strained ferrite when annealed below its critical range, as fully explained in this chapter, the formation of large ferrite grains naturally causing brittleness. This kind of brittleness is sometimes called "Stead's brittleness." No very satisfactory explanation has so far been offered to account for this greater brittleness in certain directions. It may be that the large crystalline grains of ferrite produced have nearly the same orientation and that they are so oriented as to lead to easy inter-crystalline rupture in the directions indicated.

Conclusions Regarding the Annealing of Steel. — From the foregoing considerations it appears that (1) in annealing for softness and ductility steel should be heated slightly above its critical range (Ac_3 or $Ac_{3.2}$ for hypo-eutectoid steel, $Ac_{3.2.1}$ for eutectoid and hyper-eutectoid steel) and cooled slowly, as for instance with the furnace in which it was heated, or for greater strength in air, (2) in annealing for strength and high elastic limit combined with fair ductility as well as for resistance to wear, to shock, and to fatigue, steel should be heated to slightly above its critical range followed by cooling in water, or in oil according to carbon content and requirements and reheated to some 500 to 650 deg. C. in accordance with the physical properties desired, the lower temperature yielding the greater strength but the less ductility, (3) in annealing cold-drawn wire and other cold-worked objects, especially of hypo-eutectoid steel, reheating close to but below the critical range (550 to 650 deg.) is generally sufficient for the aim in view, unless in the case of very low carbon steel so strained as to lead to ferrite growth when the temperature should be kept below 550 deg. or carried above the critical range, (4) in annealing castings they should (a) be kept several hours slightly above their critical range, or (b) be heated to a temperature considerably above the range followed by a reheating of short duration slightly above the range, or (c) be subjected to the double treatment applied to forgings, and (5) by subjecting hyper-eutectoid steel to the spheroidizing treatment its softness and ductility can be considerably increased as well as its resistance to wear.

CHAPTER XVI

THE HARDENING OF STEEL

References have already been made in these chapters to the invaluable property possessed by iron, containing a sufficient amount of carbon, of becoming extremely hard when suddenly cooled from a high temperature as, for instance, by quenching in water from a bright red heat. This operation is known as the hardening of steel. The close relation existing between the hardening of steel and its critical range, which has also been alluded to, provides the key to the rationale of the hardening operation. This operation consists of two distinct steps (1) heating to the hardening temperature and (2) cooling from that temperature.

Heating for Hardening. — In order to harden steel it is necessary first to heat it above its critical range, because it is in passing through that range that it acquires hardening power. Any attempt at hardening it by cooling it suddenly from a temperature inferior to its critical range would result in but a very slight, if any, increase of hardness. It is evident, therefore, that to possess hardening power steel must be in the condition of a solid solution since the aggregate of ferrite and cementite formed on slow cooling through the critical range cannot be hardened by sudden cooling. The metal should not be heated much above the top of its range, because in so doing we coarsen its structure as explained in previous chapters, while we do not increase, materially at least, its hardening power, and our aim in hardening should be to secure maximum hardness and finest possible structure. Quenching from a temperature greatly exceeding the critical range, moreover, increases the danger of warping and cracking the objects in the quenching bath. Nor should the steel be heated to a temperature much above its critical range and then cooled to that range before quenching, as sometimes recommended, because its structure is then likewise coarsened by the heating and slow cooling preceding the quenching. Clearly the rationale of the hardening operation consists in heating the metal just through its critical range, thus conferring to it both full hardening power and finest possible structure, and then in cooling it suddenly as soon as it emerges from its range, lest its structure be coarsened by heating above the range or by prolonged exposure at the quenching temperature. This judicious method of conducting the hardening operation is sometimes described as "hardening on a rising temperature." Let it be borne in mind that, since the position and width of the critical range vary in different steels, the most desirable quenching temperature will vary likewise. Low and medium high carbon steels should be quenched at higher temperatures than high carbon steel, for in order to acquire full hardening power they should be heated past their upper critical points, namely, Ac_3 or $Ac_{3.2}$, as the case may be.

In practice the quenching temperature should be some 20 to 50 deg. C. above Ac_1 in hardening eutectoid and hyper-eutectoid steels or above $Ac_{3.2}$ in hardening

hypo-eutectoid steel. The proper temperatures to which carbon steels should be heated for hardening purposes and which are also those generally suitable for annealing the same steels have been shown graphically in Figure 219, Chapter XV.

Heating for hardening should be slow enough to permit the steel to acquire gradually and evenly a uniform temperature throughout, and should not be too sudden as for instance by placing cold steel in red hot furnaces.

Generally speaking large pieces should be heated to somewhat higher temperatures than small pieces for hardening purposes it having been found (Benedicks and Mathews) that a higher temperature produces a quicker rate of cooling in the quenching bath. Mathews for instance states that a $\frac{3}{8}$ -in. round bar of tool steel will harden at 750 deg. C. while a $\frac{3}{4}$ -in. round bar of the same steel should be heated to 780 deg. C.

The use of lead or salt baths (chlorides and nitrates of sodium, calcium, potassium, and barium) for heating steel to the desired hardening temperature is to be commended since it promotes uniformity of temperature throughout the pieces while a suitably selected salt bath can readily be heated to, and maintained at, any desired temperature.

Cooling for Hardening. — To harden the steel the metal should be cooled very quickly from the temperatures mentioned in the above paragraphs through its critical range, generally by immersing it in a medium capable of rapidly abstracting heat from it. The increase of hardness will be the greater the higher the carbon content, at least up to the eutectoid point, and the more rapid the cooling, the latter, in turn, depending upon the size of the object hardened and the nature of the quenching bath, i.e. its power of abstracting heat from the cooling mass. It was long thought that this so to speak cooling power of the bath depended chiefly, if not solely, upon its temperature at the time of immersion and upon its heat conductivity. It was believed, for instance, that mercury was a more effective cooling medium than water because of its greater conductivity for heat, that cold water was more effective than tepid water because of its lower temperature, etc. Recent investigations appear to show, however, that the cooling power of a quenching bath is, within limits, quite independent of its actual temperature and of its heat conductivity, and even of its specific heat. Benedicks contends that it depends almost exclusively upon its latent heat of volatilization. Its temperature, however, should be low enough to prevent the adherence of vapor bubbles to the metal. In accordance with these views mercury, in Benedicks' opinion, is inferior to water while saline solutions are not superior to it. Methyl alcohol, on the contrary, is a more effective cooling medium for hardening than water. According to Le Chatelier, also, mercury is less effective than water but in his opinion because of its lower specific heat. Le Chatelier believes that the specific heat of the liquid is the most important factor influencing its value as a cooling medium, its conductivity being of secondary importance, the loss of heat taking place more through circulation than through conductivity. On the other hand Benedicks contends that the rate of flow has very little influence.

According to Mathews (1) the rate of cooling in water quenching remains quite constant up to a water temperature of 37 deg. C., (2) brine solutions not only produce a quicker rate of cooling but retain their cooling power practically unimpaired so long as their temperature remains below 65 deg. C., (3) while oil baths produce a slower rate of cooling they can be heated to considerably higher temperatures than water or brine before having their cooling power seriously diminished.

Structural Changes on Hardening. — Bearing in mind the enormous difference between the properties of hardened steel and those of the same metal unhardened, we should naturally expect to find the structure of hardened steel likewise totally different from that of unhardened steel. And so indeed it is as shown in Figure 274, in the case of hardened steel containing some 0.50 per cent carbon. To account for this structure let us remember that, initially, this steel consisted of an aggregate of ferrite and cementite which, upon being heated through its critical range, was converted into a solid solution (austenite) of carbon or carbide in gamma iron. This was necessary to impart hardening power. Had the metal been allowed to cool slowly through its critical range it would have been converted back into a mixture of ferrite and cementite. On rapid cooling, however, this transformation was prevented, at least in part, the time necessary for its completion having been denied.



Fig. 274. — Steel. Carbon 0.45 per cent. Magnified 1000 diameters. Heated to 825 deg. C. and quenched at 720 deg. (Osmond.)



Fig. 275. — Steel. Carbon 1.57 per cent. Magnified 1000 diameters. Heated to 1050 deg. C. and quenched in ice-water. (Osmond.)

A conclusive evidence that the transformation does not occur in its entirety is afforded by the absence of a marked critical range on quick cooling. If the transformation of the solid solution could be effectively prevented austenite should be the constituent of hardened steel. In the commercial hardening of steel, however, the cooling is not sudden enough to prevent at least a partial transformation of austenite, not into ferrite and cementite but into a more or less transitory form, marking the first step of that transformation and called "martensite." Very frequently the rate of cooling is not sufficiently rapid to prevent the martensite from further partial transformation into a second transition constituent known as "troostite." Martensite and troostite, then, are the ordinary constituents of commercially hardened steel. It will now be profitable to consider at some length the occurrence, nature, and properties of the three constituents chiefly concerned in dealing with hardened steel, namely, austenite, martensite, and troostite.

AUSTENITE

Nature of Austenite.¹ — Austenite is universally considered as a solid solution of carbon or, more probably, of the carbide Fe_3C in gamma iron.² All steels above their critical range are made up of this solid solution. It follows that the carbon content of austenite varies, like that of steel, from a mere trace to some 1.75 or 2 per cent. It is not, therefore, a constituent of constant composition.

Occurrence of Austenite. — While present in all steels above their critical range austenite is very rarely found in ordinary steels cooled to atmospheric temperature. This is due to the rapidity with which austenite is transformed on cooling through the critical range if not into an aggregate of ferrite and cementite, at least into some

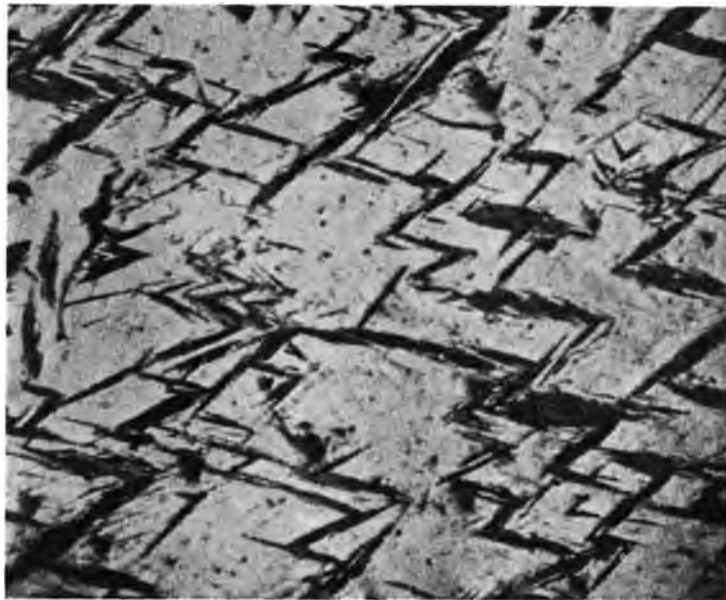


Fig. 276. — Steel. Carbon 1.57 per cent. Magnification not stated. Heated to 1050 deg. C. and quenched in ice-water. (Osmond.)

transition stages. In the commercial hardening of ordinary carbon steel the passage of the metal through its range is never sufficiently rapid to retain in the cold a small amount even of undecomposed austenite. To prevent the transformation of a portion of the austenite the conditions generally affecting the hardening of the metal must be, so to speak, greatly intensified: (1) the steel should be highly carburized, (2) quenching should be from a high temperature (1000 deg. C. or more), and (3) a very effective quenching bath should be used such as ice-cold water. In Figure 275 is shown, after Osmond, the structure of steel containing 1.57 per cent

¹ This name was suggested by Osmond in honor of the late Sir William Roberts-Austen. Austenite has also been called mixed crystals and gamma iron and by some writers, wrongly, martensite.

² Arnold believes that austenite is the carbide Fe_3C (hardening) holding in solution ferrite in hypo-eutectoid steel and cementite in hyper-eutectoid steel.

carbon heated to 1050 deg. C. and quenched in ice-water. The magnification is 1000 diameters. The dark-colored, zigzag constituent is martensite; the light matrix, or background, is austenite. The structure of the same steel, under lower magnification, is seen in Figure 276. By the drastic quenching treatment just described it is possible, in the case of high carbon steel, to retain more than one half of the steel in its austenitic condition.

The retention of austenite in the cold is greatly helped by the presence of some elements such as manganese and nickel which lower the position of the transformation range, eventually depressing it below atmospheric temperature and, therefore,

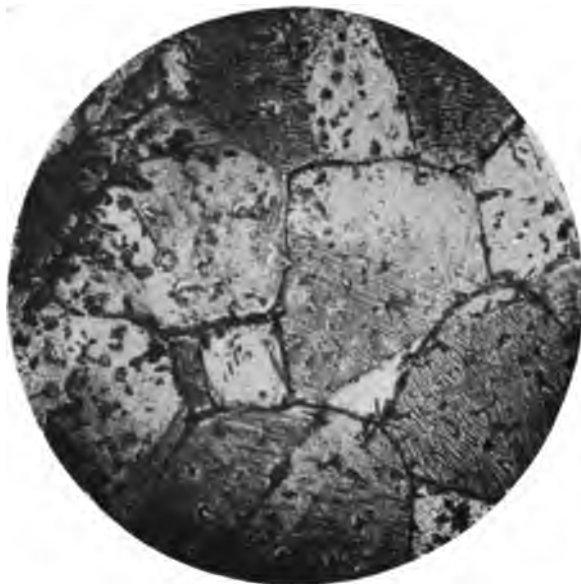


Fig. 277. — Steel. Carbon 1.60 per cent, manganese 1.00 per cent. Magnified 300 diameters. Heated to 1400 deg. C. and quenched in ice-cold water. (Robin.)

causing the steel to remain austenitic even after slow cooling. This actually takes place in the presence of some 12 per cent manganese or 25 per cent nickel. Robin, by quenching in ice-cold water from a temperature of 1400 deg. C. a very small piece of steel (1 to 2 cubic centimeters) containing 1.60 per cent carbon and 1 per cent manganese, was able to retain it in an austenitic condition (Fig. 277). Maurer, likewise, succeeded in retaining in its austenitic condition a steel containing 2 per cent manganese and 2 per cent carbon by quenching it in ice-cold water from a temperature of 1100 deg. (Fig. 278). As the manganese increases the retention of austenite becomes easier, that is, the quenching need not be so drastic nor the carbon content so high. Finally with 10 or more per cent of manganese and 1 or more per cent carbon the steel remains austenitic after slow cooling. The structure and properties of manganese steel will be considered in another chapter.

To sum up: (1) austenite is never produced in the commercial hardening of ordinary carbon steel; (2) it may be retained in the cold, however, associated with

considerable martensite in quenching very high carbon steel, from a very high temperature in ice-cold water as, for instance, by quenching steel containing not less than 1.50 per cent carbon from 1000 deg. C. or higher; (3) in the presence of 1 per cent of manganese very small pieces of very high carbon steel may be retained wholly in their austenitic condition by quenching them from a very high temperature as, for instance, by quenching in ice-cold water from 1400 deg. C. small pieces of steel containing 1 per cent of manganese and not less than 1.5 per cent carbon (Robin); (4) with increasing proportions of manganese the transformation of austenite may be prevented in steel containing less carbon and quenched from lower temperatures (Maurer); (5) manganese steels containing, for instance, 10 or more per cent manganese and 1 or more per cent carbon remain austenitic after slow cooling; (6) nickel steel containing some 25 per cent of nickel likewise remains austenitic on slow cooling.

Benedicks contends that in the preservation of austenite in carbon steel by rapid cooling an important part is played by the very great pressure to which the metal



Fig. 278. — Steel. Carbon 1.94 per cent, manganese 2.00 per cent. Heated to 1100 deg. C. and quenched in ice-cold water. (Maurer.)

is subjected, (1) because of the shrinkage of the exterior portion or outer shell on the interior and (2) because of the dilatation accompanying the change from gamma to beta iron. Were it not for this pressure Benedicks believes that the transformation of austenite could not be prevented. As an evidence of this he shows that austenitic steels produced by quenching are austenitic only in their interior, i.e. where the pressure had been greatest, the outside layers in which the pressure was small or nil being martensitic. He shows, further, that on removing by grinding the martensitic shell the austenitic core, in turn, becomes martensitic owing to the removal of the pressure exerted upon it by that shell. Again the quenching of steel cylinders surrounded by cast-iron shells resulted in the formation of austenite close to the skin of the steel cylinders owing apparently to the very great pressure exerted upon the steel by the contraction of the iron shells.

Etching of Austenite. — The etching reagents usually applied to bring out the structure of unhardened steel, namely, picric acid, nitric acid, tincture of iodine, etc., do not always yield satisfactory results in the case of hardened steel. Kourbatoff discovered a complex reagent which often produces greater contrast between the

various constituents. It is made up by mixing one part of amyl alcohol, one part of ethyl alcohol, one part of methyl alcohol, and one part of a 4 per cent solution of nitric acid in acetic anhydride and should be prepared just before use.

Heyn recommends for etching hardened steel a solution containing one part of hydrochloric acid and 99 parts of absolute alcohol. More uniform results are obtained if a weak current of electricity be passed through the solution, the samples to be etched forming the positive pole while the negative electrode may consist conveniently of a piece of sheet lead. With the assistance of the electric current the use of a very dilute aqueous solution is advisable, namely, one part of hydrochloric acid in 500 parts of distilled water.

Osmond, likewise, used successfully a solution of 10 per cent of hydrochloric acid in water by which the martensite is colored darker than austenite, the treatment requiring several minutes. Osmond writes: "There is more regularity obtained by having the specimen connected, by means of a platinum wire, with the positive pole of a bi-chromate cell, a strip of platinum placed in the acid being connected with the negative pole. In this way the specimen becomes the anode, and the platinum the cathode."

Benedicks recommends for the etching of martensite-austenitic steel a 5 per cent alcoholic solution of metanitrobenzol-sulphonic acid which always darkens martensite more than austenite. Immersions of some fifteen seconds are generally sufficient.

Structure of Austenite. — When austenite and martensite occur in the same sample the latter is generally colored darker than the former (Figs. 275 and 276). Martensite, moreover, is readily distinguishable because of its zigzag or needle shape. Some writers claim that martensite is sometimes colored less than austenite. Indeed Maurer contends that this is always so, arguing that if most photomicrographs indicate the contrary it is because the martensite had undergone a certain amount of tempering resulting in the formation of some troostite as later explained. According to this writer, in order to prevent any tempering of the martensite, and therefore the formation of dark-colored troostite, great care must be exercised in sawing, polishing, etc. To this Benedicks replies that it cannot always be so for in quenching austenite in liquid air martensite is formed which must be free from troostite and which, nevertheless, is darker than austenite. It may be asked, however, whether it is certain that the martensite produced in this way is actually free from troostite. Evidences of a more conclusive nature are needed to account satisfactorily for the shifting in the relative coloration of austenite and martensite when occurring side by side. Pure austenite is made up of polyhedral grains,¹ (see Figs. 277 and 278) which, as explained in previous chapters in connection with the structure of gamma iron, are undoubtedly made up of true crystals, small octahedra according to Osmond. It should be noted that when austenite occurs in the presence of much martensite (Fig. 275) its polyhedral structure is not brought out. Twinning is frequently observed in austenite (see Chapter V, Fig. 124), although it has been claimed that they form only after straining, especially if followed by annealing.

Baykoff succeeded in etching austenite above the critical range of the steel, that is, in a range of temperature where it is stable. He accomplished this by heating polished steel samples in a porcelain tube through which a current of hydrogen was

¹ Because of this structure Guillet and some other writers refer to steels composed of austenite as "polyhedral" steels. This does not seem advisable as it may lead to confusion, for other steels also have polyhedral structures, to wit, very low carbon (ferritic) steels.

kept circulating and by passing through it gaseous hydrochloric acid when the desired temperature had been obtained. The resulting structures were found to be polyhedral even in the presence of very little carbon, thus confirming the previous belief as to the crystalline character of austenite.

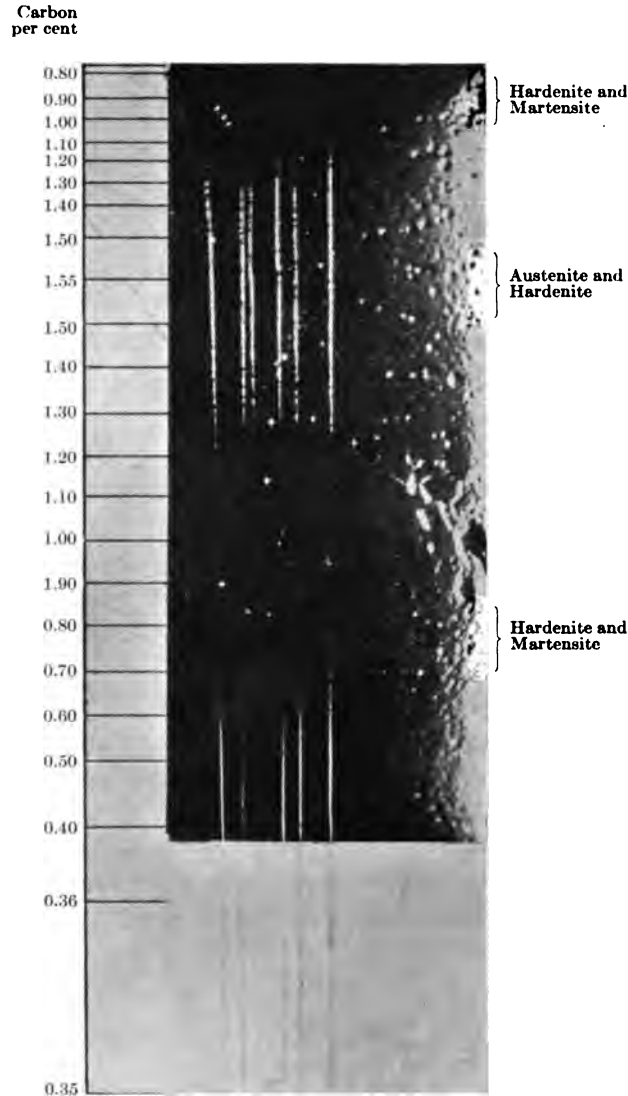


Fig. 279. — Showing the relative softness of austenite. (Osmond.)

Properties of Austenite. — Since the carbon content of austenite varies from a mere trace to nearly 2 per cent it may well be expected that its physical properties will likewise vary, i.e. that it will increase in hardness and strength and decrease in ductility as the carbon increases. Osmond has shown conclusively that austenite was softer than martensite of identical carbon content. When it is remembered that

in order to produce austenite in ordinary carbon steel all the factors generally increasing the hardness of the metal must be intensified, it is at first surprising that the energetic quenching treatment required should yield a softer metal. The conclusion must be that gamma iron is softer than beta iron. This relative softness of austenite is well shown by Osmond in Figure 279 which represents the structure of a bar of steel containing 1.55 per cent carbon in the center and a gradually decreasing amount towards the outside. This bar was heated to 1050 deg. C. and quenched in mercury at a temperature of -9 deg. C. After polishing but before etching a needle was repeatedly drawn across it from end to end with even pressure. The photograph clearly shows that the needle scratched the steel (1) where it contains so little carbon

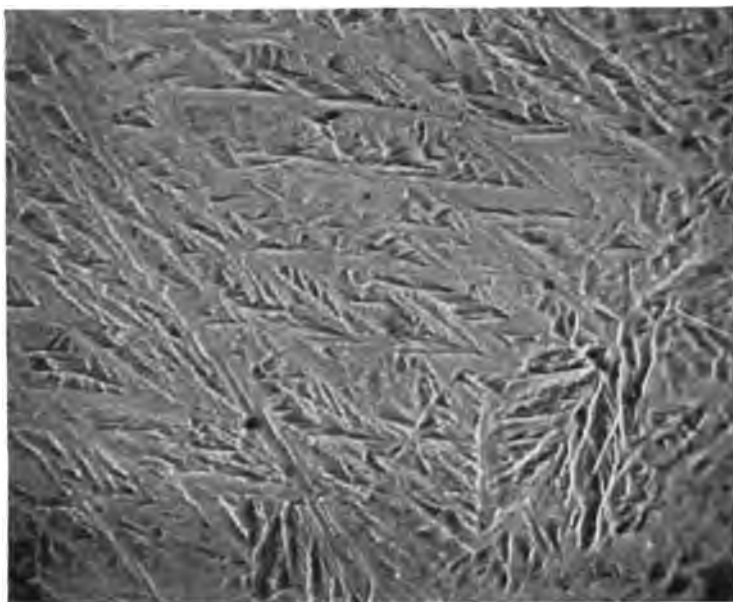


Fig. 280. — Nickel austenitic steel quenched in liquid air. Magnified 250 diameters. (Osmond.)

(0.40 to 0.60 per cent) that it was only partly martensitic and hence relatively soft, (2) in those regions which because of very high carbon content (1.30 to 1.55 per cent) were partly austenitic, and (3) that it failed to scratch it in those regions which because of a more moderate amount of carbon (0.70 to 1.20 per cent) were fully martensitic and, therefore, very hard. It is also well known that high carbon austenitic manganese steel, while extremely difficult to machine, can be readily scratched by a needle, being mineralogically softer, therefore, than high carbon, martensitic steel. Rosenhain and Humfrey have shown that above the critical range austenite (gamma iron) was much softer than beta iron. Since steel above its critical range is non-magnetic we should expect steels which remain austenitic in the cold to be non-magnetic. This we know to be the case, for manganese as well as nickel austenitic steels are non-magnetic.

Some of the physical properties of austenite may be inferred from the known

properties of austenitic steels such as manganese and high nickel steels. These are known to be very ductile (after suitable heat treatment), tenacious, of low elastic limit, to possess very high resistance to wear although their mineralogical hardness is not excessive and to be machined only with great difficulty. They have, like gamma iron, a very high electrical resistance.

It has already been pointed out that the crystallization of austenite is probably cubic, the octahedron being its prevailing crystalline form. Le Chatelier, however, believes that austenite crystallizes in the orthorhombic system with octahedral cleavage. On slow cooling through the critical range in the absence of considerable quantities of retarding elements such as manganese and nickel, austenite rejects a sufficient amount of ferrite in hypo-eutectoid, or of cementite in hyper-eutectoid, steel to assume the eutectoid composition (0.85 per cent C. or thereabout) when it is converted bodily into pearlite. This transformation is not sudden, however, several transition constituents being formed, namely, martensite, troostite, and sorbite.

It will be seen in another chapter that on tempering austenite, that is, on reheating it below the critical range of the metal it is likewise converted gradually and successively into martensite, troostite, and sorbite or according to some writers directly into troostite and then into sorbite.

Quenching nickel austenitic steel in liquid air results in the formation of martensite with increased volume causing swellings of the polished surface as shown in Figure 280.

MARTENSITE

Nature of Martensite.¹ — It is very generally believed that martensite corresponds to an early stage in the transformation of austenite in passing through the critical range. Opinions differ, however, as to its exact nature. Accepting the possibility of iron existing under three allotropic forms, namely, as gamma, beta, and alpha iron, and the carbon under two distinct conditions, namely, as the crystallized carbide Fe_3C or cement carbon and of this carbide or possibly elementary carbon being dissolved in iron, i.e. as hardening carbon, what are the probable conditions of these two constituents in martensite? Osmond and many others believe that in martensite iron is present chiefly in its beta condition, holding carbon in solution, hence the great hardness of that constituent. Since martensite is magnetic, however, it must also contain an appreciable quantity of magnetic alpha iron. This theory, which may be called the allotropic theory, was at one time widely held. Le Chatelier, not believing in the existence of beta iron, considers martensite as essentially a solid solution of carbon in alpha iron, owing its great hardness to its state of solid solution and its magnetism to the presence of alpha iron. Edwards and Carpenter contend that austenite and martensite are in reality the same constituent, namely, a solid solution of carbon in gamma iron, differing only in structural aspect, the needles of martensite resulting from the twinning of austenite caused by the severe pressure exerted upon it during rapid cooling. Kroll also speaks of martensite as representing the "mutilated structure of austenite due to twinning." Arnold believes that

¹ This name was selected by Osmond in honor of A. Martens, a distinguished German metallurgist and testing engineer.

martensite is, like austenite, the carbide Fe_2C holding in solution ferrite in hypo-eutectoid steel and cementite in hyper-eutectoid steel.

Careful consideration of the evidences at hand leads to the adoption of the first theory (Osmond's) as the one best supported. That martensite is to a great extent a solid solution seems evident from the fact that it contains a great deal of hardening, i.e. dissolved carbon, and it seems probable that beta iron is the solvent, for if gamma iron were the solvent it would not explain the greater hardness of martensite compared to that of austenite while we have good reason to doubt the power of alpha iron to dissolve carbon seeing that below the critical range, i.e. when in its alpha form, iron will not absorb carbon.

Occurrence of Martensite. — Martensite is most readily obtained through the quenching of small pieces of high carbon steel in cold water; in the case of large



Fig. 281. — Steel. Carbon 1.25 per cent. Magnified 150 diameters. Heated to 1232 deg. C. and quenched in oil. (C. C. Buck, Correspondence Course student.)

pieces, while the outside portion may be martensitic their center is likely to be partly troostitic. In low carbon steel it is more difficult still to prevent the formation of some troostite while in steel containing very little carbon free ferrite as well is likely to be present. In very high carbon steel some free cementite is generally associated with the martensite.

Etching of Martensite. — Dilute alcoholic solutions of picric, nitric, or hydrochloric acid generally bring out satisfactorily the structure of martensite but the Kourbatoff reagent, already described, sometimes yields better results. Martensite generally darkens more quickly than austenite but always remains much lighter than troostite.

Structure of Martensite. — Martensitic structures are shown in Figures 274 and 281. Osmond describes the structure of martensite as consisting of three systems of fibers, respectively parallel to the three sides of a triangle and crossing each other frequently. Osmond also states that when the metal contains less carbon the needles

are longer and more clearly differentiated, other things being equal. According to crystallographers these markings, in reality cleavages of octahedra, indicate crystallites of the cubic system and, therefore, afford an additional evidence of the cubic crystallization of austenite from which martensite is derived. Osmond and Cartaud refer to them as probable pseudomorphs of twinings due to tension, occurring in gamma iron through partial formation of the bulky beta and alpha modifications.

Properties of Martensite. — The carbon content of martensite varies from a mere trace to as much as 1 per cent, and possibly more, in very suddenly cooled hyper-eutectoid steels. In high carbon steels, however, it is difficult to prevent the setting free of much of the excess cementite even on very quick cooling. From this variation of its percentage of carbon it follows that the properties of martensite must also vary. As the carbon increases its hardness and strength increase while its ductility decreases, martensitic steels being generally hard and brittle and, therefore, unforgeable in the cold.

It will be seen in another chapter that on heating martensite below the critical range, i.e. on tempering it, it is converted first into troostite and then into sorbite.

TROOSTITE

Nature of Troostite.¹ — While most writers believe that troostite represents a condition of the steel resulting from the transformation of martensite and, therefore, a further step in the transformation of austenite, much difference of opinion exists as to its exact nature. The controversy has given rise to a very large and apparently exaggerated amount of discussion. Here, as in the case of martensite, we must consider the possibility of the iron existing in the gamma, beta, or alpha form or in two or even all three of these conditions, while the carbon may exist as cement carbon or as hardening carbon or partly as cement and partly as hardening carbon. Then the association between iron and carbon may be of the nature of an aggregate or of a solid solution or partly aggregate and partly solution or, indeed, half way between aggregate and solution, namely, resembling a colloidal solution, an emulsion, or an uncoagulated substance. Nearly every conceivable hypothesis has been suggested to account for the nature of troostite. It has been described as a solid solution of carbon or of carbide in gamma iron, in beta iron, and in alpha iron. It has also been suggested that it might be pure beta iron.

In later years, thanks chiefly to the enlightening discussions of Benedicks supported by the weighty evidence of skilfully conducted experiments, metallographists have come to regard troostite as an uncoagulated mixture of the constituents of martensite and sorbite, that is, of (1) carbide dissolved in beta iron, (2) crystallized Fe_3C , and (3) crystallized alpha iron — clearly martensite passing to sorbite. Benedicks compares it to a colloidal solution² while Arnold had previously described it as

¹ The name "troostite" was selected by Osmond in honor of the French chemist Troost.

² A colloid may be regarded as a substance passing from the state of solution to that of an aggregate or vice versa; it is no longer a solution but not yet an aggregate. To express it more scientifically, while not a true solution the particles of solvent and solute are ultra-microscopic. According to Le Chatelier so-called colloidal solutions are in no way solutions, but merely liquids holding in suspension very finely divided particles; the expression, he says, should not be used.

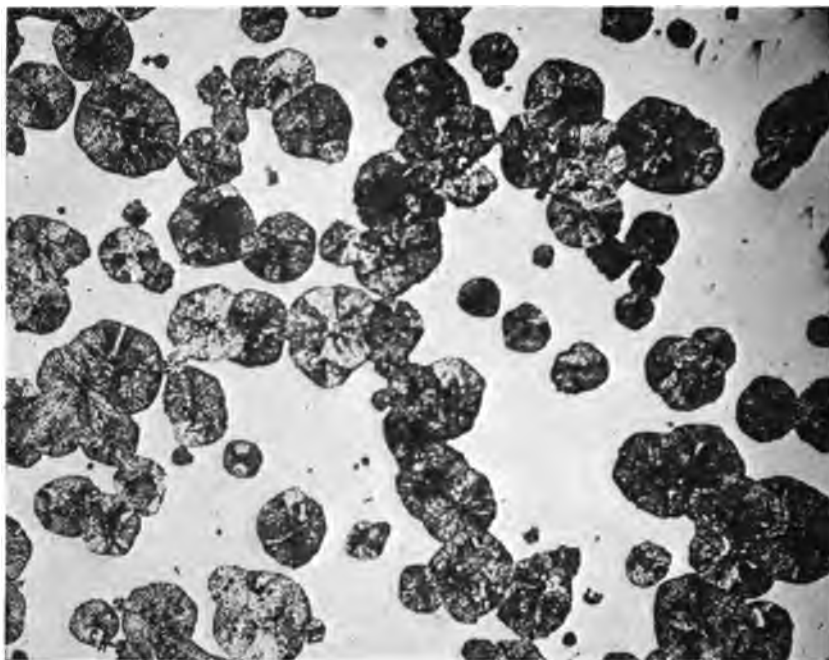


Fig. 282. — Troostite in steel containing 1.50 per cent carbon. Magnified 150 diameters.

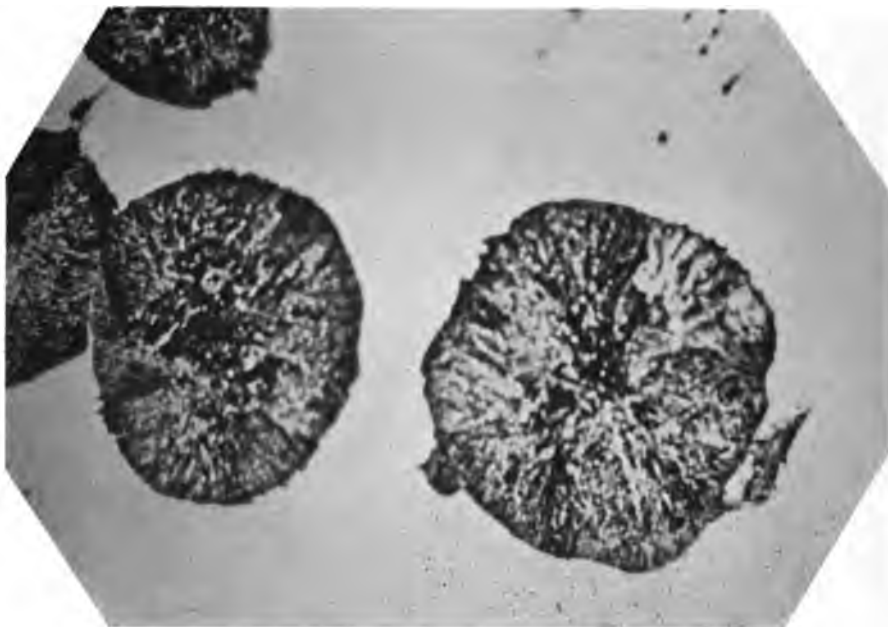


Fig. 283. — Same as Figure 282 but magnified 800 diameters.

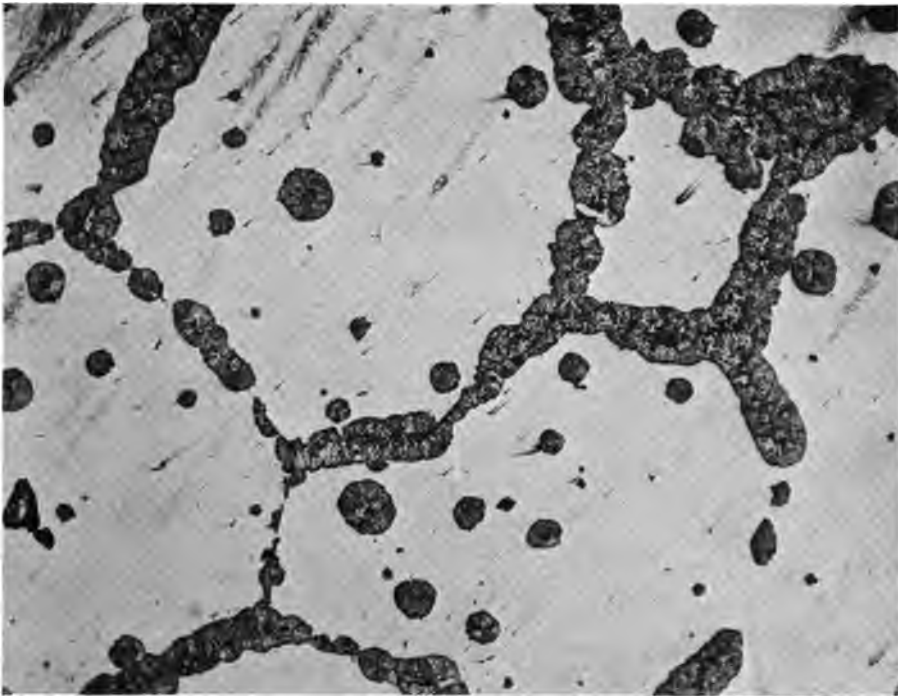


Fig. 284. — Troostite in steel containing 1.50 per cent carbon. Magnified 150 diameters.

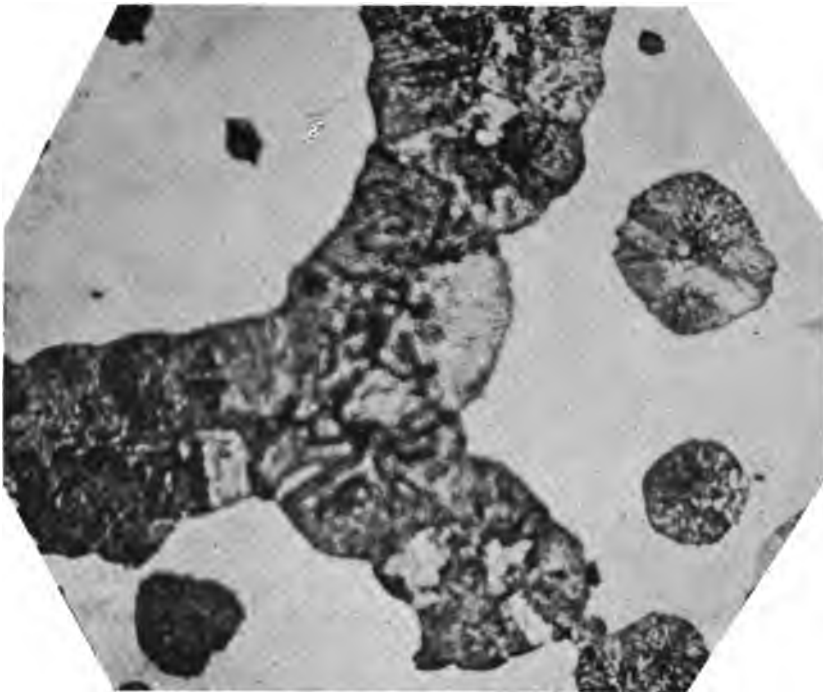


Fig. 285. — Same as Figure 284 but magnified 500 diameters.

“emulsified” pearlite.¹ The existence of considerable dissolved (hardening) carbon in troostite is proven by analysis as well as the existence of considerable crystallized Fe_3C (cement carbon). Its relatively great hardness points strongly to the presence of a considerable amount of beta iron while its magnetism demands the presence of alpha iron. Benedicks’ hypothesis is consistent with what we know of the formation of troostite and of its properties. McCance considers troostite to be amorphous alpha iron associated with carbon or a carbide, the nature of the bond between the two not being clearly stated.



Fig. 286. — Troostite and martensite-austenitic matrix in steel containing 1.50 per cent carbon. Magnified 150 diameters. (Boylston.)

In the report of the Committee on the Nomenclature of the Microscopical Constituents of Iron and Steel of the International Association for Testing Materials, troostite is defined as follows: “probably aggregate. In the transformation of austenite, the stage following martensite and preceding sorbite . . . An uncoagulated conglomerate of the transition stages.”

Occurrence of Troostite. — In order to produce troostite on cooling steel from above its critical range, it is necessary that the cooling through the range should be so regulated as to allow it to form and at the same time prevent its further transformation (into sorbite and pearlite). These conditions may prevail (1) in cooling slowly to the middle of the range, thus permitting the formation of troostite (see

¹ “Emulsified carbide present in an excessively fine state of division in tempered steels.” (1895.)

Fig. 288), and then quickly to atmospheric temperature, thus retaining troostite, and (2) in cooling through the range at a rate uniform throughout but so regulated as to cause the production and retention of troostite (Fig. 288) as, for instance, quenching large pieces in water when the central portions at least will be troostitic, or quenching smaller pieces in oil. It will be explained in the next chapter that troostite may also be produced by tempering (i.e. reheating below the critical range) austenitic and martensitic steels.

Troostite is readily produced by heating a bar of steel, containing 0.50 per cent carbon or more, white hot at one end and quenching it in water, when at some distance from the heated end the temperature must necessarily have been such as to produce troostite. This can generally be detected by means of a file, the martensitic portion of the bar being too hard to be marked while the troostitic part, although hard, can be scratched. The sorbitic and pearlitic portions are decidedly softer.

Properties of Troostite. — It will be obvious from the foregoing description of the nature and formation of troostite that its physical properties must be intermediate between those of martensite and of sorbite. For like carbon content troostite is softer and more ductile than martensite but harder and less ductile than sorbite. It will be shown that at some 400 deg. C. it begins to be transformed into sorbite.

Etching of Troostite. — Troostite is colored decidedly darker than any other constituent by the ordinary etching reagents. While dilute alcoholic solutions of nitric, picric, or hydrochloric acid yield satisfactory results, Kourbatoff's reagent is preferred by some.

Structure of Troostite. — Troostite generally occurs as dark-colored, irregular areas, representing sections through nodules generally accompanied by martensite or sorbite or both or as membranes surrounding martensite grains (Figs. 282 to 287). On deeper etching the martensitic structure of the matrix is generally revealed as shown in Figure 286. In hypo-eutectoid steel free ferrite, and in hyper-eutectoid steel free cementite, may also be present and, indeed, even well-developed pearlite (Fig. 287). Osmond describes the structure of troostite as "almost amorphous, slightly granular, and mammilated." The steel shown in Figure 287 was quenched during its critical range and contains martensite (bright), troostite (dark), sorbite (lighter than troostite and ill-defined), and pearlite (laminated).

Sorbite. — Sorbite is not, properly speaking, a constituent of hardened steel. It seems appropriate, however, to mention it again here seeing that it constitutes the connecting link between annealed (pearlitic) steels and hardened (troostite-martensitic) steels, and also because it results from the transformation of troostite, thus completing the various stages assumed by iron-carbon alloys in passing from the condition of austenite, stable above the range, to that of pearlite, stable below the range. These stages are (1) austenite, (2) martensite, (3) troostite, (4) sorbite, and (5) pearlite.

Sorbite is now generally regarded as an uncoagulated mixture of the constituents of troostite and of pearlite; it apparently contains (1) some hardening carbon, i.e. carbon or Fe_3C dissolved in beta iron, hence the greater hardness and strength of sorbite compared to the hardness and strength of pearlite, (2) a considerable quantity of alpha iron, hence its magnetism and relative softness, and (3) a considerable quantity of crystallized Fe_3C (cement carbon) as proven by analysis. While sorbite probably contains the same constituents as troostite it holds considerably less undecomposed solid solution and considerably more alpha iron, hence it is much softer

and more ductile than troostite. In other words the transformation which eventually must lead to the formation of pearlite is more advanced in sorbite than it is in troostite. The nomenclature committee, already referred to, describes sorbite as follows: "Aggregate . . . In the transformation of austenite, the stage following troostite . . . and preceding pearlite. Most writers believe it essentially an uncoagulated conglomerate of irresoluble pearlite with ferrite in hypo- and cementite in hyper-eutectoid steels respectively."

The occurrence, etching, structure, and properties of sorbite have been described in Chapters XIV and XV when it was shown that it is formed (1) in small pieces of steel cooling in the air from above their critical range, (2) in larger pieces quenched in oil from above the range, or (3) in small pieces quenched in water from near the

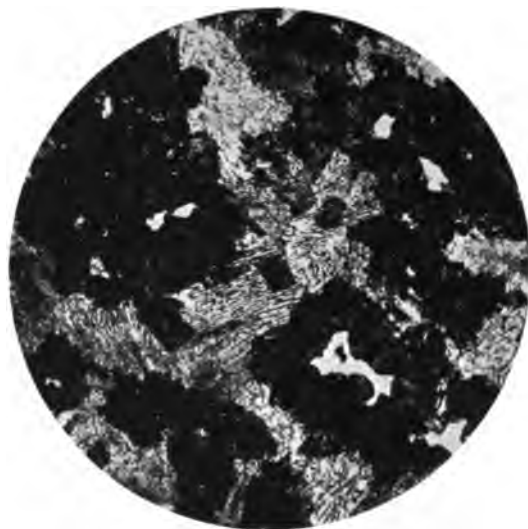


Fig. 287. — Steel. Carbon 0.80 per cent.
Quenched in the critical range. Magnified
430 diameters. (Boylston.)

bottom of the range. In other words to form sorbite we must so regulate the cooling through the critical range that it is allowed to form but prevented from further transformation (into pearlite). It will be seen in the next chapter that sorbite is also formed on tempering austenitic, martensitic, and troostitic steels.

By its physical properties sorbite occupies an intermediate position between troostite and pearlite; as previously mentioned it is stronger, harder, and less ductile than pearlite but softer and more ductile than troostite.

Troosto-Sorbite. — Kourbatoff gives the name of "troosto-sorbite" to a constituent associated with martensite and austenite in quenching, from a high temperature, steels very high in carbon. It is not clear that this constituent is more than a mixture of troostite and sorbite. We may talk of troosto-sorbite as we do of a greenish blue tint to indicate shades intermediate between green and blue, and similarly the expressions martensite-austenite, troosto-martensite, and sorbito-pearlite, or like expressions, are useful and their meanings obvious. In the report of the Committee on the

Nomenclature of the Microscopical Constituents of Iron and Steel of the International Association for Testing Materials, troost-sorbite, is thus defined: "Indefinite aggregate, the troostite and the sorbite which lie near the boundary which separates these two aggregates."

Hardenite. — The name of "hardenite" is frequently given both to austenite and to martensite of eutectoid composition,¹ i.e. to the original austenite of eutectoid steel and to the residual austenite of hypo- and hyper-eutectoid steel after rejection of the full amount of free ferrite or of free cementite. In other words the name is applied (1) to the condition of austenite in slowly cooled steels immediately preceding its conversion into martensite and (2) to the resulting martensite (necessarily of eutectoid composition if the cooling to the range has been sufficiently slow). It is unfortunate that the same term is used to designate both austenite and martensite, two apparently sharply different constituents, as it is likely to lead to confusion. Its use should be restricted to the designation of austenite of eutectoid composition. Giving it this meaning it will be apparent, as later explained, that hardenite possesses maximum hardening power and, therefore, that steel made up exclusively of hardenite, i.e. eutectoid steel, possesses maximum hardening power.

Rate of Cooling through Critical Range vs. Structure of Steel. — It has been made clear in the foregoing pages (1) that in order to retain some austenite in the cold the metal should be highly carburized and very quickly cooled from a high temperature, (2) that pearlite is produced by very slow cooling through the critical range, and (3) that in order to cause the formation of any of the three recognized transition constituents, namely martensite, troostite, and sorbite, the steel should be cooled through its critical range in such a way as to allow the formation of the desired constituent while preventing its further transformation as, for instance, (a) by cooling the metal slowly to that portion of the range in which the constituent is formed and then quickly to atmospheric temperature or (b) by cooling the metal through its range at a uniform speed but so regulated that the transformation of austenite proceeds only to the desired extent, to wit, cooling in water for martensite, in oil for sorbite.

An attempt has been made in Figure 288 to give a graphical illustration of the cooling conditions needed for the production of the various constituents of steel. Its interpretation will be obvious. The critical range, or rather the lower critical point, Ar_1 or $Ar_{3.2.1}$, is represented as covering a considerable range of temperature so as to afford the necessary room for the diagrammatical representation of the formation, within that range, of the transition constituents. The diagram indicates that as the metal cools slowly through its range it does not pass abruptly from an austenitic to a martensitic condition and then to troostite, etc., but that these transformations are, on the contrary, gradual, the following types of structure being formed, theoretically at least: austenite, austenite plus martensite, martensite, martensite plus troostite, troostite, troostite plus sorbite, sorbite, sorbite plus pearlite, and pearlite. The transformations depicted refer to eutectoid steel or to the residual austenite (necessarily of eutectoid composition) of hypo- and hyper-eutectoid steel formed on slow cooling to Ar_1 after rejection of free ferrite or free cementite. In the case of these steels, therefore, free ferrite or free cementite is present in the above structures

¹ Originally the name "hardenite" was applied by Howe to austenite and martensite of any composition (1888). Osmond used it to designate austenite saturated with carbon (1897). Both these meanings have been withdrawn by their proposers. Arnold calls hardenite the carbide Fe_3C which he believes exists above the critical range.

unless, indeed, cooling between Ar_3 and Ar_1 , or between Ar_{cm} and Ar_1 has been so rapid as to prevent their separation. While, theoretically, very quick cooling from a to atmospheric temperature should retain the steel in its austenitic condition, even under the most favorable conditions, this can be done but partially, considerable martensite being produced. Cooling slowly to m and then quickly should produce martensite, while slow cooling to t or s followed by quick cooling should produce, respectively, troostite and sorbite. Slow cooling to p , followed or not by quick cooling, results in the formation of pearlite. Slow cooling to intermediate points between m and t or t and s , etc., should, theoretically, cause the formation of martensite and troostite, troostite and sorbite, etc.

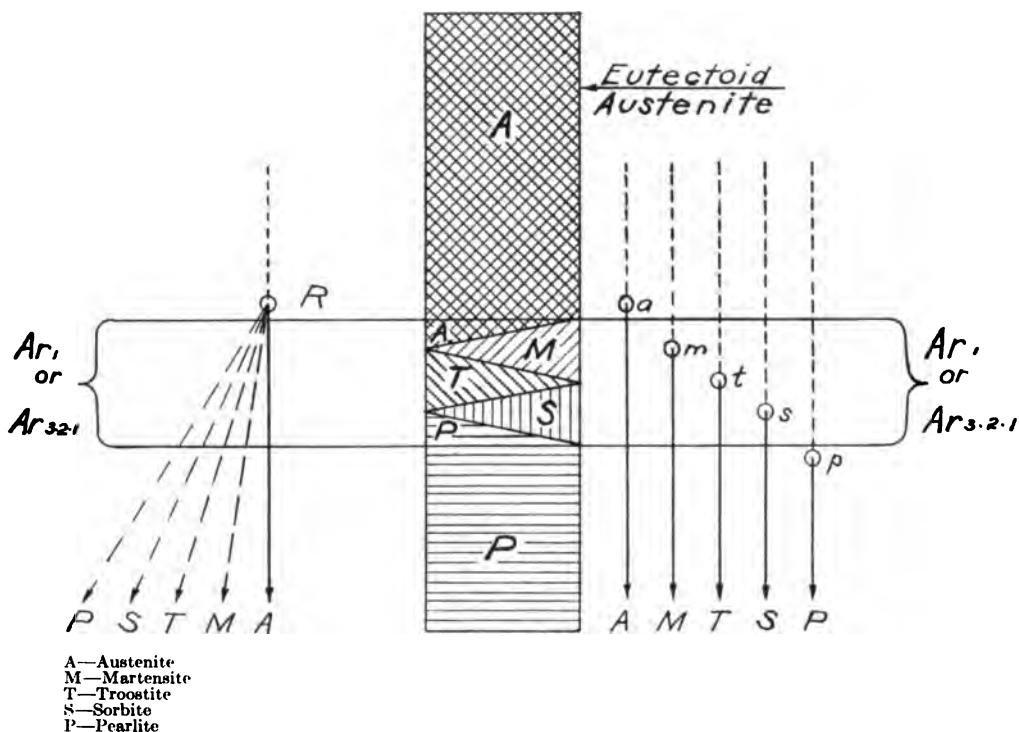


Fig. 288. — Diagram depicting the formation of austenite, martensite, troostite, sorbite, and pearlite in steel cooling through its critical range.

These conditions may be realized in the same piece of steel by heating one end of a steel bar, preferably of eutectoid or hyper-eutectoid composition, well above the critical range and quenching the whole bar in ice-cold water. It is evident that, since at the time of quenching the temperature of the bar decreased gradually from the hot to the cold end, a portion of the bar must have been quenched while in the martensitic condition, another while in the troostitic condition, etc. The preparation and microscopical examination of longitudinal sections through the center of the bar should reveal the existence of the various constituents indicating as many stages in the transformation of austenite.

On the left of the diagram five lines starting from the point R above the critical

range represent coolings through the range at different speeds as, for instance, (1) very quickly in ice-cold water, (2) quickly in water, (3) less quickly in oil, (4) slowly in air, and (5) very slowly in furnace, resulting, respectively, in the formation of austenite (or rather austenite and martensite), martensite, troostite, sorbite, and pearlite or, more frequently, of mixtures of two or even three of these constituents.

These conditions may be realized in the same piece of metal by heating a steel bar of considerable cross section (not less than 1 inch in diameter) and preferably of eutectoid or hyper-eutectoid composition to a temperature well above the critical range and quenching it in water. The cooling should be rapid enough to cause the formation of martensite near the outside of the piece while the cooling of the center should be so slow (because of the size of the bar) as to permit the formation of pearlite. Between the martensitic shell and the pearlitic core the metal should be composed of the other transition constituents, that is starting from the center, of sorbite and then of troostite. The microscopical examination of a cross section through the bar should reveal this gradual change of structure from center to outside.

The formation of a transition constituent through the tempering of a constituent representing a less advanced, and therefore less stable, stage of transformation has already been alluded to and will be considered at greater length in the next chapter.

Are the Transition Stages Distinct Constituents? — It would appear from our consideration of the formation of the transition constituents that they must represent as many stages in the *progressive* transformation of austenite and that sharp lines of demarcation between them are not to be expected or, rather, that they must be linked together by an unbroken chain of transition stages just as the blue and yellow colors are connected through an unbroken series of bluish, greenish, and yellowish shades. This logical inference, however, is not supported by microscopical evidences in the cases of austenite, martensite, and troostite for these constituents are sharply differentiated from each other whenever they occur together. Stages or structural conditions representing the gradual transformation of austenite into martensite or of martensite into troostite are not observed; it is as if these transformations had actually taken place by rather sudden steps.

The transformations of troostite into sorbite and of sorbite into pearlite, on the contrary, appear to be very gradual and easy to follow. In other words while troostite, sorbite, and pearlite are readily distinguishable, each having marked characteristics of its own, structural arrangements are frequently observed which undoubtedly correspond to intermediate stages.

The five constituents of steel, resulting from various modes and rates of cooling, might be compared to a spectrum of five elementary colors, i.e. violet, blue, yellow, orange, and red, with gaps existing between the first three (our austenite, martensite, and troostite) while the third and the fifth, yellow and red (troostite and pearlite) are closely linked together by the fourth, orange (our sorbite), and an infinity of intermediate shades.

Metarals and Aggregates. — Howe suggests dividing all microscopical constituents of iron and steel into (1) metarals and (2) aggregates.

These he describes as follows: "Metarals, true phases like the minerals of nature. These are like definite chemical compounds, or solid solutions, and hence consisting of definite substances in varying proportions . . . Aggregates, like the petrographic entities as distinguished from the true minerals. These mixtures may be in definite

proportions, i.e. eutectic or eutectoid mixtures (ledeburite, pearlite, steadite) or in indefinite proportions (troostite, sorbite)."¹ Under these two headings the constituents of iron-carbon alloys would be classified as follows:

Metarals: ferrite, cementite, austenite, graphite.

Aggregates: pearlite, sorbite, troostite, ledeburite, steadite.

Opinions differ as to the nature of martensite; if it is a solid solution it is a metaral, if not it must be classified with the aggregates. Should we recognize the existence of solid colloidal solutions, it is not clear whether these should be grouped with the metarals or should form a distinct class between the metarals and the aggregates.

Hardening Eutectoid Steel. — It will now be profitable to consider separately the hardening of eutectoid, hyper-eutectoid, and hypo-eutectoid steel. In hardening eutectoid steel the metal should be heated through its critical range, i.e. through its single critical point $Ac_{3.2.1}$. By so doing we confer upon it full hardening power and finest possible structure. The steel should then be cooled from that temperature as promptly as possible avoiding heating much above the range or long exposure at any temperature above the range, as either procedure would tend to increase the grain size of the metal. A temperature of some 775 to 825 deg. C. will generally be, therefore, the best temperature to which to heat and from which to cool eutectoid steel for the purpose of hardening. By this treatment the steel passes from a finely austenitic to a finely martensitic or troostite-martensitic condition.

Hardening Hyper-Eutectoid Steel. — Let us assume a steel containing 1.25 per cent carbon and, therefore, composed approximately of 93 per cent of pearlite and 7 per cent of free cementite. Upon heating this steel through its lower point $Ac_{3.2.1}$ its 93 per cent of pearlite are converted into 93 per cent of austenite possessing hardening power, but the metal still contains 7 per cent of free cementite deprived of hardening power. If we heat it past its upper point Ac_{cm} the free cementite is absorbed and the whole mass becomes austenitic. A little reflection will show, however, that the steel should be quenched as soon as it rises above the point $Ac_{3.2.1}$, because we then produce, theoretically at least, 93 per cent of fine-grained martensite while retaining, to be sure, the original 7 per cent of cementite, but as this constituent is harder than martensite its presence adds to, rather than takes away from, the hardness of the quenched metal. Should we, on the contrary, heat to above Ac_{cm} before quenching the whole mass would be converted into martensite but it would be less hard if anything than the metal quenched at a lower temperature while its structure would be coarser and the danger of cracking the objects in the quenching bath would be greater. The best hardening temperature for hyper-eutectoid steels, therefore, is the same as that for eutectoid steel, namely, some 775 to 825 deg. C.

The following treatment has been described for hardening hyper-eutectoid steel: Heat above A_{cm} to cause the absorption of the free cementite and cool in boiling water or lead, thereby preventing the excess cementite from re-forming although the quenching is too mild to produce cracks or serious distortion; the piece then should be reheated slightly above Ac_1 and quenched in the usual way.

¹ Howe further writes: "Many true minerals, such as mica, felspar, and hornblende, are divisible into several different species. Such minerals are definite chemical compounds, in which one element may replace another. Others, such as obsidian, are solid solutions in varying proportions and in these also one element may replace another. Metarals like minerals differ from aggregates in being severally chemically homogeneous."

The structure of a properly hardened hyper-eutectoid steel is shown in Figure 289. Like hardened eutectoid steel it consists of very fine martensite.

Hardening Hypo-Eutectoid Steel. — Let us take a steel containing some 0.50 per cent carbon and exhibiting therefore the points A_1 and $A_{3.2}$. Such steel is made up of 60 per cent of pearlite and 40 per cent free ferrite. Upon heating it through its Ac_1 point the pearlite is converted into austenite, so that at this temperature some 60 per cent of the mass of the metal is endowed with hardening power. Should we quench this steel, therefore, as soon as it rises above its lower critical point but 60 per cent of its bulk would be hardened; it would still retain 40 per cent of soft ferrite. If, on the contrary, the heating be carried to just above $Ac_{3.2}$ the free ferrite is absorbed by the austenite and the whole mass becomes *hardenable*. Upon quenching



Fig. 289. — Steel. Carbon 1.10 per cent. Magnified 100 diameters. Quenched in water from above its critical range. (Boylston.)

the steel from that temperature its entire bulk may be converted into martensite or troostite-martensite, according to rate of cooling. While this martensite will not be quite as hard as the martensite produced by quenching from just above Ac_1 the metal as a whole will be harder and of a more uniform and finer structure because of the absence of free ferrite, or at least of any considerable amount of it. It follows from these considerations that for the purpose of hardening, hypo-eutectoid steel should be quenched from just above its upper critical point, namely, $Ac_{3.2}$ or Ac_3 (825 to 925 deg. C. according to carbon content). Hypo-eutectoid steel containing very little carbon, say less than 0.25 per cent, cannot be very materially hardened by the ordinary quenching methods because of the large amount of soft ferrite which it contains in excess of the eutectoid ratio and which cannot be retained in solution, even on very quick cooling (see Chapter XV, Fig. 229). The structure of steel containing about 0.25 per cent carbon and quenched in water is shown in Figure 290.

Steel of Maximum Hardening Power. — From the above considerations it will be obvious that the hardening of steel consists in preventing the formation of relatively soft pearlite and in causing, instead, the formation and retention of hard martensite or troostite or, more often, of both. It follows from this that the steel possessing maximum hardening power must be that steel which in slow cooling would contain most pearlite, namely, eutectoid steel. It does not, of course, mean that quenched eutectoid steel is harder than quenched hyper-eutectoid steel but merely that the increased hardness produced by quenching is greatest in the case of eutectoid steel. Quenched hyper-eutectoid steel is harder than quenched eutectoid steel because of the presence in the former of some free cementite or of more highly carburized mar-



Fig. 290. — Steel. About 0.25 per cent carbon.
Heated to 1000 deg. C. and quenched in water.
Magnified 100 diameters. (W. B. Byers in the
author's laboratory.)

tensite but the difference of hardness between the two steels is greater before quenching.

Hardening Large Pieces. — In hardening pieces of considerable cross section it is evident that the central portions will not cool as quickly as the outside and will not, therefore, be as hard. Indeed the center may cool so slowly that it will fail to harden at all. The limitation of the hardening process, as applied to large pieces, will, therefore, be evident. It is seldom desirable, however, to harden large pieces to their very core. When large steel objects are to be hardened, as for instance in the case of armor plates, superficial hardness only is desired, or at least hardness penetrating to but a relatively small depth, and this is readily secured through the case-hardening process.

The influence of mass in cooling for hardening is well illustrated by Le Chatelier who states that a steel bar containing 1.00 per cent carbon and measuring 10 mm. in diameter when quenched in water is wholly martensitic whereas the same steel in the form of bars 50 mm. in diameter is entirely troostitic after quenching, intermediate sizes being mixtures of martensite and troostite.

Hardening and Tempering in One Operation. — A peculiar but frequent way of hardening tools consists in heating the tool to the proper temperature and then cooling quickly to a black heat only that portion of it which should be hard, while keeping the other portion out of the bath and, therefore, at a high temperature. Upon withdrawing the tool from the bath the heat stored away in the hot portion diffuses to the cooled portion which is in this way reheated, that is, tempered, as later explained, the amount of tempering being regulated at will by again quenching the metal as soon as the desired tempering color has been obtained.

CHAPTER XVII

THE TEMPERING OF HARDENED STEEL

Steel that has been hardened by rapid cooling from above its critical range, as explained in the preceding chapter, is often harder than necessary and generally too brittle for most purposes besides being under severe internal strain. In order to relieve the strains and decrease its brittleness, that is, to toughen it without very material diminution of hardness, the metal is generally "tempered," that is, reheated to a temperature considerably below its critical range. This operation is called tempering because it somewhat mitigates or tempers the effects of the previous hardening treatment. Mathews calls attention to the importance of tempering *immediately* after hardening, lest the severe strains existing in the steel result in the destruction by breaking of expensive tools.

Tempering Temperatures. — The hardening of steel causes increased hardness, brittleness, and elastic limit, all of which are somewhat lowered by the tempering operation. The effect of tempering begins to be noticeable at about 100 deg. C. and increases in intensity as the temperature rises, until finally at some 600 deg. the metal assumes again the physical properties characteristic of the unhardened condition. The temperature to which hardened steel should be heated for tempering varies, therefore, with the use to which it is destined. If it is desired to retain the greatest possible hardness, necessarily with its accompanying brittleness, the steel should be reheated but slightly above 200 deg. C. as, for instance, in tempering razor blades when extreme hardness is essential and brittleness relatively immaterial. If, on the contrary, considerable toughness is indispensable, at the necessary sacrifice of some hardness the steel should be tempered to some 300 deg. C. or even to a higher temperature. The great majority of tools are tempered between 200 and 300 deg.

Tempering Colors. — Hardened steel objects subjected to tempering being generally quite bright and their heating being generally conducted in an oxidizing atmosphere, very thin films of oxides form upon their surfaces. The colors of these films vary with the temperature, that is, to each tempering temperature corresponds a certain color, and blacksmiths generally depend upon these colors for the tempering of their tools, the use of pyrometers for this operation being far from general. According to Howe the tempering colors and corresponding temperatures are as follows:

Pale yellow	220 deg. C. or	428 deg. F.
Straw	230 " " "	446 " "
Golden yellow	243 " " "	469 " "
Brown	255 " " "	491 " "
Brown dappled with purple	265 " " "	509 " "
Purple	277 " " "	531 " "
Bright blue	288 " " "	550 " "
Pale blue	297 " " "	567 " "
Dark blue	316 " " "	600 " "

In order that the tempering colors may be plainly seen the steel objects should be smooth and bright, preferably polished.

Time at Tempering Temperature. — It is the common belief that once the desired temperature is obtained, as indicated by the color, little is to be gained by maintaining the steel at that temperature any length of time on the ground that it will not result in producing additional tempering. The tempering of steel has been compared to the releasing of a spring permitting a certain structural rearrangement, that is, a certain tempering of the metal at any temperature but not more. To produce additional tempering the temperature must be increased, that is, the spring must be further released. Recent investigations, however, have shown that the maintenance of hardened steel at a certain tempering temperature often does produce additional tempering effect. It was further ascertained that the color, instead of remaining unchanged at any given temperature, advances in the tempering color scale as it would with increasing temperature. In other words, the tempering colors, contrary to the view generally held, are not an absolute criterion by which to judge of the temperature of the steel, since they vary with the length of time during which the steel is kept at any temperature. These experiments seem to show, however, that the amount of tempering effected is closely related to the color, that is, that to each shade corresponds a certain amount of tempering. It should, however, be borne in mind that these colors, with the corresponding tempering they imply, may be obtained in two ways, (1) through short exposure at a certain temperature and (2) through longer exposure at lower temperatures. The same amount of tempering, for instance, would result (a) from heating hardened steel to 288 deg., when its color is bright blue, followed by immediate cooling and (b) from heating it to 255 deg., when its color is brown, and maintaining it at that temperature until its color becomes bright blue. Unless baths kept at constant temperatures are used, however, it is evident that in practise the steel should be quenched as soon as the desired color is produced and while its temperature is rising, because it is simpler and more convenient to produce that color on a rising temperature than by maintaining the metal at a constant temperature.

Some writers doubt the existence of so close a relation between the color and the resulting tempering. According to Barus and Strouhal to each tempering temperature corresponds a maximum tempering effect, which is the more quickly reached the higher the temperature. At 100 deg., for instance, the maximum effect was not obtained after one hour although maintaining the steel at that temperature two more hours had but little additional effect. At 200 deg. the maximum effect was obtained in ten minutes, while at 300 deg. one minute was sufficient.

Mathews tempered 3 hardened pieces of the same steel in a salt bath at 422 deg. C. keeping them at that temperature respectively for 8, 20, and 40 minutes and obtained Brinell hardness numbers of 425, 390, and 340 respectively.

Rate of Cooling from Tempering Temperature. — Once the desired amount of tempering is effected, as indicated by the color or otherwise, the rate of cooling to atmospheric temperature appears to be quite immaterial. In practise the piece is generally quenched, merely for convenience. The theory is that while by keeping the metal at a certain temperature its tempering may be carried farther, on cooling tempering ceases, for the spring is now tightened, to use the simile already referred to, so that the rate of cooling is without influence.

Hardening and Tempering Combined. — A method of hardening and tempering combined, frequently employed when but one end of a tool must be hardened, as in the case of chisels and drills, has been described in the preceding chapter. It consists

in heating the tool above its critical range, quenching that portion only which is to be hard, removing it from the bath, and allowing the heat stored in the unquenched portion to heat by conduction the quenched part until the desired temper color is obtained, when it is again quenched lest the tempering be carried too far.

Explanation of the Tempering of Steel. — The theories accounting for the tempering of steel will be considered in the next chapter together with the hardening theories. It will suffice for the present to point out that hardened steel is generally considered to be in an unstable condition and, therefore, eager to return to a more stable form and actually undergoing this change whenever given an opportunity, that is on raising its temperature. At atmospheric temperature the passage of an unstable martensitic condition into a more stable troostitic or sorbitic form is prevented by the rigidity of the metal. A slight heating, however, produces some plasticity and such transformation takes place to a small extent. On increasing the temperature the rigidity diminishes further and the transformation advances. The tempering of hardened steel, in other words, is due to its transformation from an unstable condition to one more stable. It will be seen that at some 600 deg. C. the metal assumes a stable condition, i.e. is fully tempered.

Tempering Austenitic Steels. — It has been explained in the preceding chapter that austenite, martensite, troostite, and even sorbite were the constituents formed in hardened steel according to the rapidity with which the metal is cooled through and below its critical range. It will now be instructive to consider separately the tempering of steels having these different types of structure.

Austenitic carbon steel, as already stated, is not a commercial article, as it requires for its production, at least in the absence of a large proportion of manganese, the presence of much carbon, an excessively high quenching temperature, and a quenching bath at a very low temperature. And even when these conditions prevail, only one half or so of the bulk of the steel can be retained in an austenitic condition, the other half being martensitic. The tempering of austenite should, nevertheless, be considered. Since in austenitic steel the condition of the metal stable only above the critical range has been retained in the cold, it follows that cold austenitic steel must be in a very unstable condition. At atmospheric temperature the rigidity of the metal is so great that a return to a more stable form is not possible but, on heating it very slightly, sufficient plasticity is produced to permit a partial transformation of austenite. This partial transformation, theoretically at least, should result in the formation of martensite, troostite, and sorbite in the order named as the tempering temperature increases. This has been depicted in I, Figure 291. In this diagram it is shown (1) that as soon as austenite is heated above atmospheric temperature it begins to be converted into martensite, (2) that it is entirely converted into martensite at 200 deg. C., (3) that in heating above 200 deg. martensite begins to pass to troostite, (4) that at 400 deg. the transformation of martensite into troostite is complete, (5) that above 400 deg. troostite is gradually converted into sorbite, (6) that at 600 deg. C. the transformation of troostite into sorbite is complete, and (7) that the sorbite condition is the final condition acquired by hardened steel when reheated close to, but below, its critical range. While it is certain that lamellar, i.e. true pearlite, cannot be formed by reheating hardened steel, it has been shown that long heating of sorbite near the critical range, that is, between 600 and 700 deg. C., will result in the formation of granular pearlite brought about as explained in another chapter by the spheroidizing of the cementite. The tempering of austenite depicted in I, Figure 291, rep-

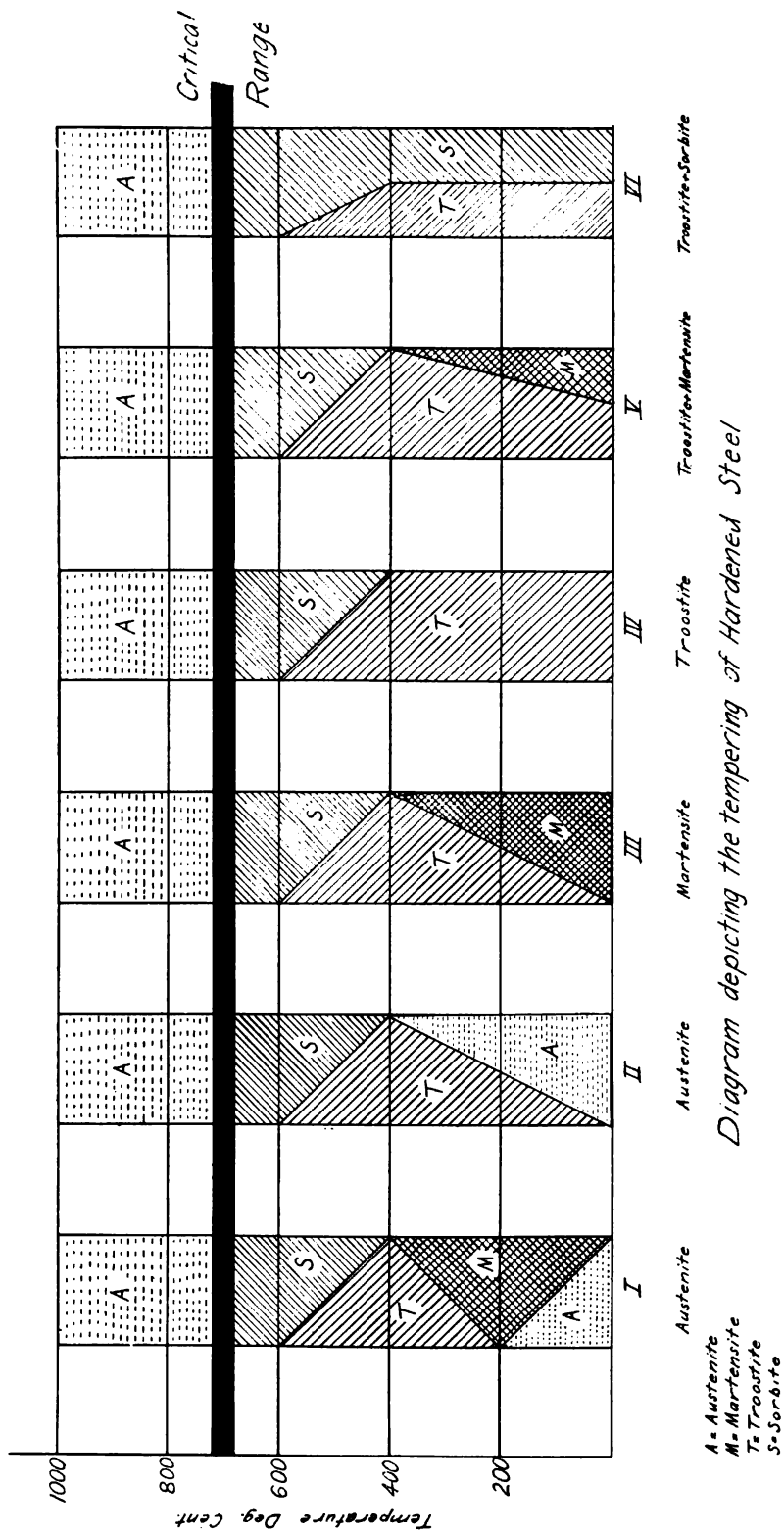


Fig. 291.

resents the transformation which, according to theoretical consideration, should be expected to take place. Most observers, however, report that on tempering austenite it is at once converted into troostite as soon as the rigidity of the steel has been sufficiently relaxed, the martensitic stage not being assumed. This is shown diagrammatically in II, Figure 291. Here, again, it is indicated that at 400 deg. the steel is entirely troostitic and at 600 deg. entirely sorbitic. Benedicks thinks that it is quite possible that austenite is first transformed into martensite but that the resulting martensite is so readily and quickly converted into troostite that its short existence easily escapes observation. His belief is based upon the following considerations: (1) the austenite retained in high carbon steel by very sudden cooling is subjected to great pressure caused by the accompanying martensite having been formed with considerable dilatation, (2) on reheating this martensite-austenitic steel the martensite is first converted into troostite, because this transformation taking place with contraction is readily induced, (3) once this transformation started, the pressure upon the austenite is released and this constituent, in turn, passes first to the martensitic stage (with increase of volume) and then quickly to the troostitic stage (with decrease of volume) the martensitic condition being of so short duration as to escape detection readily.

Tempering Martensitic Steel. — It has been shown that martensite is generally present in commercially hardened steel. Since this constituent represents a partial transformation of austenite it follows that it must be more stable than austenite at atmospheric temperature. It is sufficiently unstable, however, to be readily converted first into troostite and then into sorbite on tempering as indicated in III, Figure 291. At 400 deg. the transformation of martensite into troostite is complete, while at 600 deg. troostite is replaced by sorbite. Bearing in mind the physical properties of martensite, troostite, and sorbite, it will be readily understood why, on tempering martensitic steel, its hardness gradually decreases while it becomes less brittle and indeed quite ductile if made sorbitic.

Tempering Troostitic Steel. — Commercially hardened steel frequently contains large proportions of troostite. The tempering of troostite is depicted in IV, Figure 291. This constituent being decidedly less unstable than martensite requires greater plasticity, i.e. a higher temperature, before being transformed into a still more stable condition. Experimental evidences seem to show that the tempering of troostite, i.e. its transformation into sorbite, requires a temperature of at least 400 deg. and that at 600 deg. the transformation is complete. Since in practice the tempering of steel is seldom carried above 300 deg. it would seem as if steels made up of troostite do not need to be tempered, being sufficiently tough. There seems to be no reason to doubt the accuracy of the above inference. Commercially hardened steels, however, are generally either entirely martensitic or, more frequently, partly martensitic and partly troostitic and are in need of tempering because of the large proportion of the excessively hard and brittle martensite they usually contain.

Tempering Troostite-Martensitic Steel. — In V, Figure 291, the tempering of hardened steel containing both martensite and troostite has been depicted. It is assumed that the martensite present begins to be converted into troostite as soon as the temperature of the metal rises, while the transformation of the troostite into sorbite begins only at 400 deg.

Tempering Troostite-Sorbitic Steel. — From the diagram used to illustrate the tempering of steel it will be apparent that sorbite is relatively so stable a constituent

that its transformation into pearlite cannot be effected below the critical range or, in other words, that it cannot be tempered. Indeed sorbitic steels not being hardened steels need not be considered in connection with the tempering operation. A graphical representation of the tempering of troostite-sorbitic steel, however, has been included in Figure 291. It shows that such steel remains unchanged until its temperature reaches 400 deg. when the troostite it contains begins to be transformed into sorbite, the transformation being, as usual, complete at 600 deg.

Osmondite. — It has been shown that on tempering hardened steel it is entirely converted into troostite at about 400 deg. C. Below that temperature some martensite remains in the structure, while above it some sorbite is present. To the condition of steel when made up wholly of troostite Heyn gives the name of "osmondite." It will be apparent that osmondite does not represent a new constituent but merely a condition assumed by the steel at a certain temperature and the wisdom of giving a specific name to that condition may well be questioned.

Troostite is more readily colored by the usual etching reagents than any other constituent of steel, from which it follows that steel made up exclusively of troostite, i.e. in the osmondite condition, must exhibit maximum coloration. Again Heyn has shown that the solubility of steel in dilute sulphuric acid increases with the amount of troostite present, being maximum in steel tempered to about 400 deg. C. From these observations Heyn described osmondite as a constituent of steel characterized by maximum solubility in acids and by maximum coloration under the action of acid metallographic reagents. In the report of the Committee on the Nomenclature of the Constituents of Iron and Steel of the International Association for Testing Materials osmondite is described as follows: "Probably aggregate. That stage in the transformation of austenite at which the solubility in dilute sulphuric acid reaches its maximum rapidity. Arbitrarily taken as the boundary between troostite and sorbite . . . The following hypotheses have been suggested, none of which has substantial experimental foundation: (1) A solid solution of carbon or an iron carbide in alpha iron; (2) The colloidal system of Benedicks in its purity, troostite being this system while forming at the expense of martensite, and sorbite being this system coagulating and passing into pearlite; (3) The stage of maximum purity of amorphous alpha iron in the way to crystallizing into ferrite."

Structural Changes on Slow Cooling, Quick Cooling, and Reheating. — It seems helpful and instructive to depict graphically in a single diagram the structural changes taking place in eutectoid steel (1) on slow cooling through its critical range, (2) on quick cooling through that range, and (3) on reheating quickly cooled (hardened) steel above the range. The changes indicated in I (Fig. 292) show, as already explained, that steel, on cooling slowly through the critical range, is converted successively into martensite, troostite, sorbite, and pearlite. On heating the same steel from below to above the range the same changes would take place but in the reverse order. In II the steel has been cooled through the range at such speed that martensite was formed but prevented from further transformation, hardened martensitic steel being produced. The reheating of this martensitic steel is depicted in III. Below the range martensite is gradually converted first into troostite and then into sorbite. On entering the range the steel remains sorbitic but on further heating the sorbite is converted back into troostite and then into martensite. Near the top of the range austenite begins forming, the transformation being complete as the steel emerges from its range. Similar structural transformations would take place in subjecting

hypo-eutectoid and hyper-eutectoid steels to like treatments, but free ferrite or free cementite would generally be present.

Microstructure of Hardened and Tempered Steel. — The structural changes corresponding to the transformations taking place on tempering hardened steel described in the foregoing pages are not always readily detected by microscopical examination. This is due to the fact that, structurally speaking, these changes are often pseudomorphic changes, the crystalline forms of the original constituent or

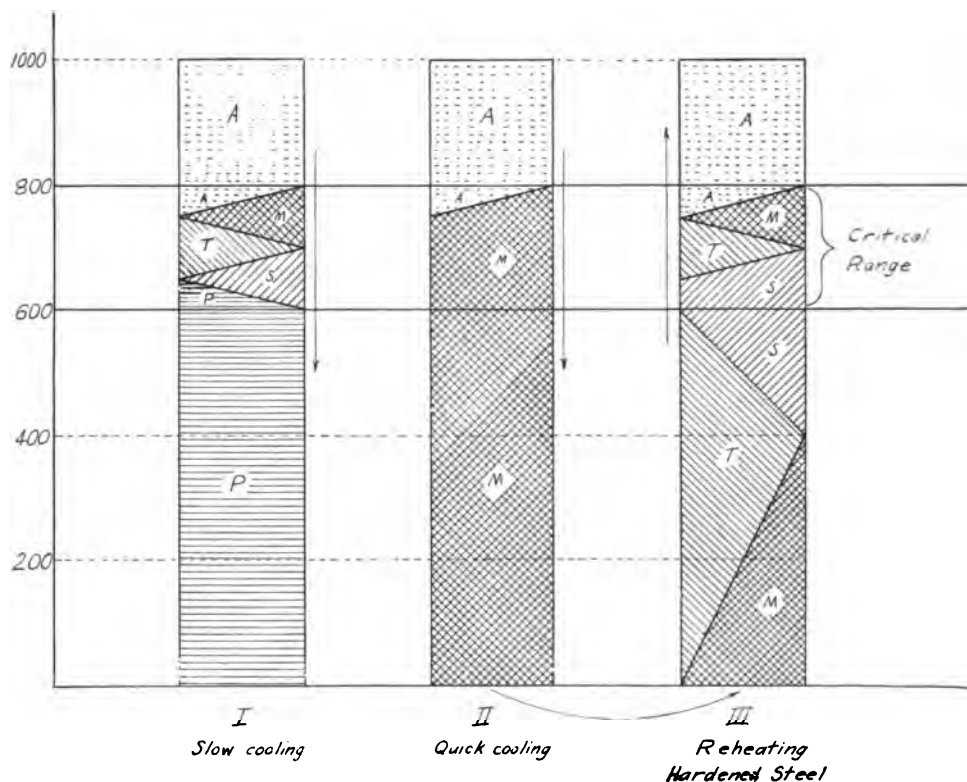


Fig. 292. — Diagram depicting the constituents formed (I) on slow cooling, (II) on quick cooling, and (III) on reheating hardened steel.

constituents having been retained, although the nature of the crystals themselves has been altered.

Referring to pseudomorphism Dana writes: "The crystalline forms under which a species occur are sometimes those of another species." Bayley defines pseudomorphs as bodies possessing forms borrowed from another substance, or as a body possessing the form of one substance and the chemical and physical properties of another. In the formation of a pseudomorph the material of the original substance is replaced by the new substance but its external form remains unchanged.

According to Heyn the following appearances are observed in the case of eutectoid steel:

(1) After hardening but before tempering: martensite with well-developed needles remaining uncolored after an immersion of 10 minutes in a solution of 1 per cent of hydrochloric acid in alcohol.

(2) After tempering between 100 and 200 deg.: martensitic structure unchanged but colored yellow or brown.

(3) After tempering to 275 deg.: the needle structure becomes coarser and recalls mixtures of austenite and martensite, one of the constituents remaining uncolored, the other assuming a dark coloration.

(4) After tempering to 405 deg.: the needles have disappeared and the sample appears dark and mottled suggesting a mixture of two relatively dark constituents; this is troostite.

(5) After tempering to 500 deg.: the light areas becomes more abundant.

(6) After tempering to 600 deg.: irregular meshes are observed rounded and light, partially surrounded by a darker network which appear to stand in relief.

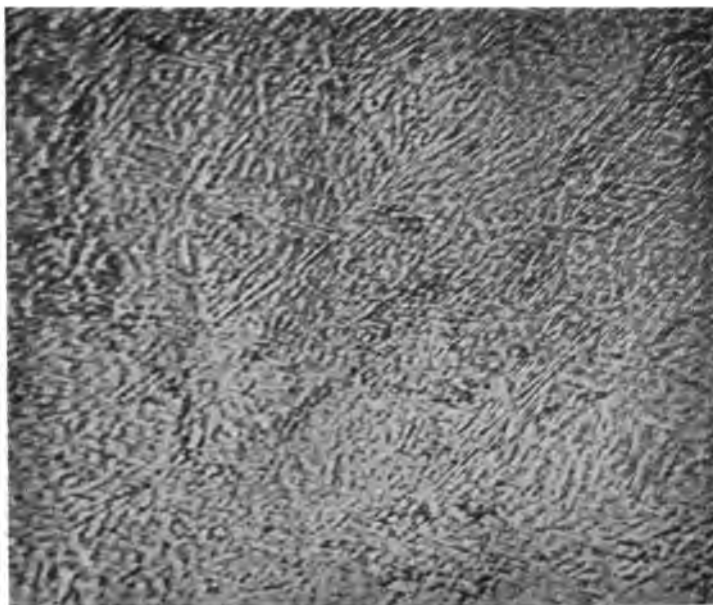


Fig. 293. — Steel. Carbon 0.45 per cent. Magnified 1000 diameters. Heated to 825 deg. C., quenched from 720 deg., and tempered between blue and brown (275 deg.?). (Osmond.)

Photomicrographs of the structure of hardened and tempered steels are reproduced in Figures 293 and 294. The structure of hardened steel reheated to 600 deg. has been shown in Figure 231, Chapter XV.

Carbon Condition in Tempered Steel. — It is generally admitted that the combined carbon present in steel may exist under two different conditions, (1) as hardening carbon, that is as carbon or the carbide Fe_3C *dissolved* in iron, and (2) as cement carbon, that is as the *crystallized* carbide Fe_3C or cementite. It is further believed (a) that pearlite is quite, if not altogether, free from hardening carbon, (b) that martensite contains, for a given steel, the maximum amount of hardening carbon that can be produced and retained in that steel by the ordinary hardening operation and

(c) that on tempering martensite the amount of hardening carbon decreases as the tempering temperature increases, while the proportion of cement carbon increases correspondingly. Heyn, however, found that on analyzing the residue remaining on dissolving, in dilute sulphuric acid, hardened eutectoid steel tempered below 400 deg. it contained no carbon in the form of the carbide Fe_3C , that is no cement carbon. For the carbon remaining in the residue and which, in his opinion, is different from cement carbon, Heyn suggested the notation Cf. Not until a temperature of 400 deg. had been reached on tempering was cement carbon detected in the residue. Heyn infers from these observations (1) that troostite contains no cement carbon, its residual carbon being in the hypothetical Cf condition, (2) that osmondite contains the



Fig. 294. — Steel. Carbon 0.50 per cent. Magnified 500 diameters. Heated to 850 deg. C., quenched in water, reheated to 400 deg., and quenched in water. (W. H. Knight in the author's laboratory.)

maximum amount of Cf carbon, and (3) that sorbite must be formed, that is, the steel must be tempered above 400 deg. in order to produce cement carbon. Heyn further argues that the deep coloration produced on etching hardened and tempered steel is caused by the separation of Cf carbon, being, therefore, maximum in osmondite, that is, when the steel contains nothing but troostite.

Osmond very appropriately remarks that it is not necessary in order to explain Heyn's results to admit the existence of a new form of carbon, it being quite possible that the Cf carbon of Heyn is cement carbon, that is, Fe_3C so finely divided when formed below 400 deg. that it is readily decomposed by the acid, while above 400 it becomes coarser and, therefore, resists better the action of the acid.

Decrease of Hardness on Tempering. — According to Boynton the decrease of hardness taking place on tempering is gradual up to 350 deg., quite sudden between 350 and 550, and nil above 550 deg.

Heyn found the following values for the loss of hardness on tempering expressed in per cent of the original increase produced by the hardening operation:

at 100 deg.	2.5 per cent	at 400 deg.	70.0 per cent
" 200 "	14.0 " "	" 500 "	87.5 " "
" 300 "	41.0 " "	" 600 "	97.5 " "

Heyn also observed that the loss of hardness takes place most quickly at 300 deg.

Heat Liberated on Tempering. — In hardening steel the cooling through and below its critical range is so rapid that the transformation of austenite which would have taken place had time been given can proceed but partially, namely, to the martensitic or troostite-martensitic stage. The heat which would have been generated had the transformation been complete remains latent in hardened steel. On tempering, however, the partially suppressed transformation is permitted to proceed farther, this return to a more stable condition being accompanied by some evolution of heat. According to Osmond this latent heat can be made apparent by dissolving hardened steel in double chloride of ammonium and copper when it evolves more heat than unhardened steel.

Heyn made some careful determinations of the heat generated on tempering hardened steel. The greater acceleration in heating hardened steel was made apparent by the differential method, using as neutral bodies similar steels in their pearlitic, that is unhardened, condition. It was observed that the heat generated on tempering is maximum at 360 deg.

H. Schottky reports that when placing hardened steel in water vapor its temperature rises several tenths of a degree above that of the vapor, from which it must be inferred that even at so low a temperature some tempering must take place. He finds that the evolution of heat increases with the carbon content up to a certain maximum and then decreases. The following results were obtained.

CARBON PER CENT	QUENCHING TEMP. DEG. C.	TEMPERATURE OF STEEL PIECES
0.54	1000	100.15
0.89	1100	100.35
1.22	1000	100.55
1.43	1300	100.33
1.10	1350	100.20

CHAPTER XVIII

THEORIES OF THE HARDENING OF STEEL

Many theories have been put forward to explain the hardening of steel through sudden cooling from a high temperature. They may be divided into two classes, (I) the "retention" theories and (II) the stress theories. The retention theories include (A) the solution theories, (B) the amorphous iron theory, and (C) the carbon theories. Two solution theories at least have been proposed, (a) the beta iron theory and (b) the alpha iron theory, while two carbon theories should be mentioned, (a) the hardening carbon theory and (b) the subcarbide theory. The stress theories include (A) the early theory, (B) the interstrain theory, and (C) the twinning and amorphous iron theory. This classification of the hardening theories is given below in a tabular form, as well as the names of their proposers.

(I) Retention theories	{	(A) Solution theories	{	(a) Beta iron or allotropic theory	Osmond		
		(B) Amorphous iron theory	{	(b) Alpha iron theory	H. Le Chatelier		
				(C) Carbon theories	{	(a) Hardening carbon theory	Humfrey
						(b) Subcarbide theory	Arnold
(II) Stress theories	{	(A) Early stress theory			André Le Chatelier		
		(B) Interstrain theory			McCance		
		(C) Twinning and amorphous iron theory			Carpenter and Edwards		

Retention Theories. — The retention theories claim that in hardening steel a condition or set of conditions existing normally above its critical range is retained unchanged in the cold or but partially changed because of the rapid cooling through and below the critical range. In other words, such very quick cooling through the range denies the necessary time for the transformations to take place, at least fully, and a condition is preserved in the cold which is stable only above or within the critical range. According to these theories hardened steel, therefore, is in an unstable condition, hence the possibility of tempering it. That the transformations which would have taken place on slow cooling through the range are suppressed, partly at least, in hardening is made evident by the absence of critical points during very rapid cooling or by the appearance of feeble points only at greatly lowered temperatures. Other evidences of the partial suppression of the transformations are afforded (1) by the condition of the carbon in hardened steel which is different from the condition of that element in unhardened steel, (2) by the evolution of heat taking place on tem-

pering hardened steel as explained in Chapter XVII, and (3) by the structure of hardened steel.

To assume that hardened steel owes its hardness to the suppression, partial at least, of the transformations taking place on slow cooling through the critical range is, therefore, both natural and logical.

When we come to look into the nature of the constituents stable above or within the range, which on being retained in the cold impart extreme hardness to steel, we find very great differences of opinion among competent authorities.

Solution Theories. — Many writers believe that hardened steel is in the condition of a solid solution, quick cooling through the range having prevented the formation of the ferrite-cementite aggregate. This is strongly supported by microscopical and other evidences. They all agree that the solution consists of carbon dissolved in iron but different views are held in regard to the condition of the carbon and of the iron. While it is now the general belief that the carbide Fe_3C rather than elementary carbon is dissolved in iron, some think that in hardened steel the iron is chiefly present as beta iron, while others believe that it exists mainly in the alpha condition.

Beta Iron or Allotropic Theory. — This theory put forward with great vigor and brilliancy by Osmond, championed first by the late Roberts-Austen and later by Howe and many other eminent metallurgists, contends that in hardened steel iron is present chiefly in the beta condition. It is often referred to as the allotropic theory of the hardening of steel. It should be borne in mind, however, that Osmond's allotropic theory of iron and his allotropic theory of the hardening of steel are two different conceptions. One may believe in the former without being an adherent of the latter. The allotropic theory of iron claims that iron exists in at least two and probably in three allotropic forms. No one doubts the allotropy of iron although some writers believe that only two allotropic forms, namely gamma and alpha iron, have been shown to exist. The allotropic theory of the hardening of steel claims (1) that in hardened steel carbon, or more probably the carbide Fe_3C , is in solution chiefly in beta iron, hence its hardness, beta iron being very hard, (2) that hardened steel contains alpha iron, hence its magnetism, alpha iron being the only allotropic form under which iron is magnetic.

While the allotropists regard the retention of beta iron as the chief cause of the hardening of steel, they do not ignore the very important part played by carbon. They realize that the presence of carbon is essential to the retention of iron in its hard allotropic form, for in the absence of carbon it is not possible to harden iron. It is customary to compare this action of carbon in preventing the transformations to that of a brake, the more carbon the more powerful the brake action, hence the harder the steel because of the retention of a larger quantity of beta iron. They believe, however, that the hardness of quenched steel increases with the proportion of the beta iron it contains rather than with the proportion of carbon. In other words, that if it were possible to retain the same amount of beta iron with less carbon or even in the complete absence of carbon the metal would be equally hard. The allotropists do not claim that steels hardened in the ordinary way, that is, martensitic steels, are absolutely free from gamma iron. Evidences are lacking to settle this point. Again the allotropists do not deny that the internal pressure created by the transformation of austenite into the more bulky martensite may contribute to the hardness of the metal.

Summing up, in the light of this theory, the hardening of steel by rapid cooling is thus explained: (1) the bulk of the iron passes from the gamma to the beta condition, hence the great hardness produced, (2) some of the beta iron is further transformed into alpha iron, hence the magnetism of hardened steel, (3) a large proportion of the carbon or more probably of the carbide Fe_3C remains dissolved in the beta iron, the presence of this dissolved (hardening) carbon in hardened steel being proven by chemical analysis, (4) the internal pressure created by the transformation of austenite into martensite, that is, of gamma into beta iron, may contribute to the final hardness. Osmond's theory of the hardening is, therefore, based on the belief (1) in the existence of beta iron and (2) in the hardness of beta iron.

On tempering hardened steel Heyn found that 70 per cent of the increased hardness produced by the hardening operation were lost in tempering below 400 deg., the remaining 30 per cent being possibly due, according to Osmond, to the internal pressure already alluded to. He further observed that hardening (dissolved) carbon did not begin to be converted into cement carbon (crystallized Fe_3C) until a temperature of 400 deg. was reached. Steel then loses most of its hardness while its carbon remains in the hardening condition. From this coexistence of softness and hardening carbon it logically follows that steel does not owe its hardness to the presence of hardening carbon, and that the presence of allotropic beta iron remains the only possible explanation. This conclusion is further supported by the fact that on tempering steel it is chiefly below 400 deg. that heat is liberated and this liberation must necessarily be ascribed to the iron returning from the beta to the alpha condition.

Alpha Iron Theory. — Le Chatelier and Guillet believe that on quick cooling through the critical range the allotropic transformation of iron from its gamma to its alpha condition is not prevented but that the steel remains, nevertheless, in the condition of a solid solution, hardened steel in their opinion being a solid solution of carbon (or of the carbide Fe_3C) in alpha iron owing its hardness to its state of solution and its magnetism to the presence of alpha iron. This view is based chiefly upon these writers' belief that the point A_2 is not an allotropic point and that therefore beta iron does not exist.

Amorphous Iron Theory. — According to J. C. W. Humfrey: "The hard structure which can be produced in carbon steels by quenching and in certain alloy steels by normal cooling, is due to the presence of a hard amorphous solution of a iron and iron carbide, which solution may be compared to Beilby's amorphous phase formed by overstrain.

"To explain the formation of this amorphous phase the author advances a theory that the passage of a substance from one allotropic modification to another of different crystalline form involves the temporary formation of an amorphous state, corresponding to the liquid phase of the modification about to be formed. In steels such a change occurs at A_2 ; and if, due to sudden cooling or to the presence of certain alloyed elements, the change-point is lowered to a temperature below that at which crystallization in the viscous mass becomes difficult, then the amorphous form will be retained in a metastable form in the cold."

Carbon Theories. — The carbon theories contend that the hardness of rapidly cooled steel is due primarily to the retention in the cold of a very hard condition of the carbon normally stable only above the range, the allotropic transformation of iron playing no, or but an unimportant, part in the phenomenon. As supporting their claims they point to the fact that carbonless iron cannot be hardened and that

the more carbon present the greater the increased hardness produced by quick cooling, at least up to the eutectoid carbon ratio.

These theories differ in regard to the exact condition of the carbon thus retained by quenching and imparting great hardness to the metal.

The Hardening Carbon Theory. — It was held for many years by the majority of writers that hardened steel owed its hardness to the presence of hardening carbon, a form of carbon stable only above the range but which could be retained, in part at least, by quick cooling. This belief rested on the apparent difference existing between the condition of the carbon in hardened and in unhardened steels as proven by dissolving them in cold dilute acids when a large proportion of the carbon of hardened steel escapes as hydrocarbons, whereas nearly the totality of the carbon of unhardened steel remains as a residue which, upon being analyzed, is found to consist of the carbide Fe_3C . As to the exact nature of hardening carbon, vague, conflicting, and often extraordinary statements appeared, it being claimed by some, for instance, that hardening carbon was carbon in a diamond-like condition. It is at present believed by most that hardening carbon is carbon (or more probably the carbide Fe_3C) dissolved in iron, its escape as hydrocarbons upon being subjected to the action of dilute acids being due to its extremely fine state of division. If this be the nature of hardening carbon, the hardening carbon theory becomes, of course, a solution theory.

It is obvious that carbon as such, no matter how great its hardness, could not impart extreme hardness to steel in which it may be associated with 199 times its weight of soft ferrite as, for instance, in steel containing 0.50 per cent carbon. The contention that it is not carbon, as such, which is retained by quick cooling but a very hard carbide constituting the whole or a large part of hardened steel is not, of course, open to the same objections. This is the claim of the subcarbide theory.

The Subcarbide Theory. — Arnold contends that eutectoid steel above its critical range exists as the carbide Fe_{24}C , a chemical compound containing about 0.89 per cent carbon. This carbide which he calls "hardenite" is very hard and being retained by quick cooling imparts hardness to quenched steel. In hypo-eutectoid steel some ferrite and in hyper-eutectoid steel some cementite are dissolved in this subcarbide. It follows from this theory that austenite and martensite correspond to different structural appearances of the same constituent, namely, the carbide Fe_{24}C when of eutectoid composition, the same carbide plus ferrite or cementite in hypo- or hyper-eutectoid steel. This theory is purely of a speculative character, the existence of the carbide Fe_{24}C not being supported by a single direct evidence. It is, moreover, strongly opposed by the universally accepted theory of metallic alloys which holds that eutectic and (eutectoid) alloys immediately before their formation are not definite chemical compounds but liquid or solid solutions. On forming, whether or not it implies a change of state, the solution is transformed into an aggregate of the solute and solvent, ferrite and cementite in the case of iron-carbon alloys. The breaking up at a certain critical temperature of a definite chemical compound, as demanded by Arnold's theory, into a eutectoid aggregate of the elements of that compound is contrary to our firmly established knowledge of the mechanism of the formation of such aggregates. It implies a return to Guthrie's original error.

The Stress Theories. — In cooling steel quickly from above its critical range it is subjected to two kinds of stresses, (1) stresses due to the shrinkage of its outer shell on its interior and (2) stresses due to the transformation with increased volume of gamma into beta and alpha iron. The existence of the strains resulting from these

stresses have been claimed to account satisfactorily for the hardening of steel by sudden cooling. It was argued long ago, for instance, that the hardening of steel by sudden cooling might be due to the metal being in a severely strained condition, because of the quicker cooling of the outer layers, these layers through their contraction exerting a severe pressure upon the central portion of the steel objects. The advocates of this theory pointed to the increased hardness resulting from cold-working steel as a proof that severe straining produces hardness. Some went as far as to claim that cold-worked steel and hardened steel are practically in the same physical condition, the quenching of steel producing, so to speak, an internal cold-working (straining) of the metal. They seem to have overlooked the enormous difference between the relatively small increase of hardness produced by cold-working and the hardness resulting from quenching. In the fact that both cold-working and hardening increase the elastic limit and decrease the ductility they found additional support for their view. According to Osmond the belief once held that cold-working causes an allotropic transformation is now abandoned. While it is not unreasonable to assume that the strained condition of the metal adds to its hardness it is hardly thinkable that the sudden and very great increase of hardness produced by quick cooling is due altogether to this straining. If it were so the outer layers of quenched steel implements should not be hard and razor blades could not be hardened. Again, it is impossible to reconcile this theory with the fact that it is necessary to quench steel from above its critical range in order to harden it, for one cannot conceive why, if the steel be quenched slightly below the range, the strain created in the quenching bath would be so slight as to have no hardening effect, whereas quenching from a temperature but a few degrees higher would produce very severe straining. Finally, if the contraction of the outer layers due to their rapid cooling can induce such hardening strains in the case of steel, it is surprising that a similar phenomenon is not observed in the case of other metals. The internal strains resulting from the transformation of gamma into beta iron (austenite into martensite) with increased volume afford a more acceptable explanation of the hardening of steel. It was offered long ago and has recently been revived and presented in a more scientific way, notably by André Le Chatelier, Charpy, and Grenet. It is argued that on quick cooling the allotropic transformations take place, partially at least, at a temperature so low that the metal lacks the necessary plasticity to yield to the severe stress excited by these transformations, remaining, therefore, severely strained. It becomes internally "écroui," as the French express it. Here again, however, it would seem as if the outer layers should not be strained and should, therefore, remain soft, which of course is contrary to facts. Nor is the failure of carbonless iron to harden satisfactorily explained by this theory.

Grenet believes that in hardened steel the allotropic transformations are complete, that is, that its iron exists only in the alpha condition but so severely strained (*écroui*) as to be very hard. He rests his belief chiefly on his assertion that on quick cooling the dilatations indicative of the allotropic transformations are not suppressed and that the metal does not remain non-magnetic. He overlooks the claims of the advocates of the retention theories, so strongly supported, that the transformations are not *completely* suppressed, hence the occurrence of a dilatation and of magnetism. When they are completely prevented, as in austenitic steels, the metal neither expands nor becomes magnetic on cooling.

The liberation of heat observed on tempering hardened steel points to a return to

a more stable condition, supporting, therefore, the retention theories and opposing the stress theories.

Interstrain Theory. — Andrew McCance believes that on cooling steel quickly from above its critical range the whole of the carbon remains in solution while the bulk of the gamma iron is converted into alpha iron. This alpha iron however is in an interstrained condition owing to the fact that its crystalline units have been denied the time to assume an homogeneous orientation and the hardness of quenched steel is due to this interstrained condition. It is further contended that strained iron cannot be described as amorphous because if it were amorphous it could not be ferromagnetic, interstrain in his opinion being a better term to describe its condition. McCance writes: "On quenching steel, the carbon is retained in solution and in turn it retains a proportion of the iron in the gamma condition, but the majority of the iron is alpha iron. At the quenching temperature the crystal grains had the crystalline symmetry of gamma iron, and the gamma iron retained in the quenched state by the carbon will form an internal network in these original steel grains. The rest of the iron will be transformed, and will form crystal units of alpha symmetry, but these will be prevented by lack of time, by internal friction, and by the gamma iron network, from arranging themselves to form homogeneously oriented alpha iron crystals. The *alpha iron will be in a condition similar to interstrain, and great hardness will result.*"

Twinning and Amorphous Iron Theory. — Carpenter and Edwards argue that in quenching steel very severe internal stresses are set up causing internal straining of the metal which in turn results in the formation of numerous twins and of hard amorphous layers. The markings of martensite in their opinion correspond to these twins. Edwards writes: "That the material is internally strained is evident from the facts which have been published, namely, the metallic crystals are broken up into an exceedingly large number of twin lamellæ. Further we believe that the hardness produced by quenching is brought about by crystal twinning and possibly direct slipping and the formation of amorphous layers as a result of the internal deformation."

Tempering and the Retention Theories. — The tempering of hardened steel, as already explained, is readily accounted for by the retention theories on the ground that the metal being in an unstable condition is ever eager to assume a more stable form, implying a return, partial at least, of the iron to the alpha condition and of the carbon to the cement condition. On heating the steel but slightly above atmospheric temperature its rigidity is sufficiently diminished to permit a slight transformation of this kind, the higher the temperature the more pronounced of course being its tempering.

Tempering and the Stress Theory. — The stress theory, likewise, satisfactorily accounts for the tempering of hardened steel on the ground that upon slight reheating the internal strains are sufficiently released to produce an appreciable decrease of the specific effects of hardening, namely decrease of hardness, of strength, of elastic limit and increased ductility.

Summary. — It seems quite possible, even probable, that the various theories, while apparently antagonistic, bring each their contribution to the elucidation of the problem. Should we not believe with the allotropists that the hardness of steel is due chiefly to the retention of a large quantity of a hard allotropic variety of iron, possibly amorphous and of the dissolved or hardening carbon of the carbonists? Should we not with the advocates of the stress theories believe in the hardening influence of

the strains created on quick cooling (a) because of the shrinkage of the outer layers of the metal and (b) because of the expansion accompanying the transformation of gamma into beta iron? None of these theories alone gives a fully satisfactory explanation: Beta iron cannot be retained in the absence of carbon and if it could be it is not certain that it would be intensely hard; the presence of intensely hard carbon or iron carbide as the chief cause of hardening is contrary to evidences; the strained condition of hardened steel alone does not account satisfactorily for its extreme hardness; Le Chatelier's contention that quickly cooled steel is hard although its iron is in the soft alpha condition because of its being in a state of solution is open to objection; Arnold's theory that hardened steel owes its hardness to the retention of a hard subcarbide of iron lacks experimental support and is scientifically untenable.

The author concluded as follows a recent paper on "Metallography and the Hardening of Steel" presented at the International Engineering Congress in September, 1915, in San Francisco:

"It will be obvious from the foregoing that the many recent attempts at arriving at a satisfactory explanation of the hardening of steel are based on one or more of the following conceptions: (1) existence of a hard allotropic variety of iron, (2) existence of solid solutions involving the occurrence of so-called "hardening" carbon, and (3) existence of strains in quenched steel causing or not an amorphous condition of the iron.

"It will likewise be obvious that no theory so far presented fully satisfies our craving for a scientifically acceptable explanation of the many phenomena involved.

"It would seem as if the methods used to date for the elucidation of this complex problem have yielded all they are capable of yielding and that further straining of these methods will only serve to confuse the issue, a point having been reached when this juggling, no matter how skilfully done, with allotropy, solid solutions, and strains is causing weariness without advancing the solution of the problem. The tendency of late has been to abandon the safer road of experimental facts and to enter the maze of excessive speculations, in which there is great danger of some becoming hopelessly lost.

"The conclusion seems warranted that new avenues of approach must be found if we are ever to obtain a correct answer to this apparent enigma."

CHAPTER XIX

THE CEMENTATION AND CASE HARDENING OF STEEL

The affinity of iron for carbon is so great that when heated to a sufficiently high temperature in contact with some suitable carbonaceous matter it readily absorbs carbon. If the heating be protracted (several days) and the amount of carbon absorbed considerable, the operation is known as "cementation" and the resulting metal as "cemented," "converted," or "blister" steel, or in Sheffield, England, as "blister bar," while if the treatment be of relatively short duration (a few hours) and the absorption of carbon in consequence superficial, it is called "case hardening."

Cementation is generally applied to wrought-iron bars which are afterwards melted (crucible process) and shaped into finished articles by casting or forging, while case hardening is applied directly to finished objects generally of low carbon steel. The purpose of cementation is to introduce carbon into wrought iron, thereby converting it into steel, the subsequent treatments (melting, forging) producing a uniform distribution of the carbon, whereas the purpose of case hardening is to manufacture steel objects with hard skins or cases while retaining their soft and tough centers or cores.

The quantity of carbon thus absorbed by iron at a high temperature but below its melting-point depends chiefly upon (1) the composition of the iron or steel subjected to carburizing, (2) the carburizing temperature, (3) the length of time at that temperature, and (4) the nature of the carburizing material.

Composition of the Iron or Steel Subjected to Carburizing. — It is probably true that the smaller the proportion of carbon in the iron the more eagerly will it take up carbon, from which it follows that as the carburizing proceeds, that is, as the metal becomes more highly carburized, additional introduction of carbon requires progressively longer time, the metal acting in this way not unlike a solution approaching its saturation point.

In the cementation process bars of very pure wrought iron and in "case hardening" steel objects containing at the most 0.20 per cent carbon are subjected to the carburizing treatment. The steel should not generally contain over 0.40 per cent of manganese lest the case be too brittle. The presence of certain elements appear to hinder the carburizing operation while others facilitate it.

According to Guillet the absorption of carbon is favored by those special elements which exist as double carbides such as manganese, tungsten, chromium, molybdenum, and opposed by those which form solid solutions with iron such as nickel, silicon, and aluminum.

Carburizing Temperature. — While it has been claimed that iron below its critical range will absorb some carbon this absorption, if taking place at all, is very slow, from which it is logical to infer that alpha iron has very little, if any, dissolving power

for carbon. In order to produce quick and intense carburization the iron should be in its beta or, more probably, in its gamma condition, and steel, therefore, in the condition of a solid solution. Cementing and case-hardening operations must consequently be conducted above the critical range of the iron or low carbon steel treated, that is, at a temperature exceeding 825 deg. C. It is also certain that the higher the temperature the quicker will carbon be absorbed and the deeper will it penetrate into the steel, that is, the deeper the "case." At Sheffield, England, where the cementation process is used more extensively than anywhere else the carburizing temperature is in the vicinity of 950 to 1000 deg. Most case-hardening treatments are probably conducted in the vicinity of 900 to 950 deg. C.

Time at Carburizing Temperature. — The amount of carbon absorbed, and therefore the thickness of the case as well, increases, of course, with the length of the

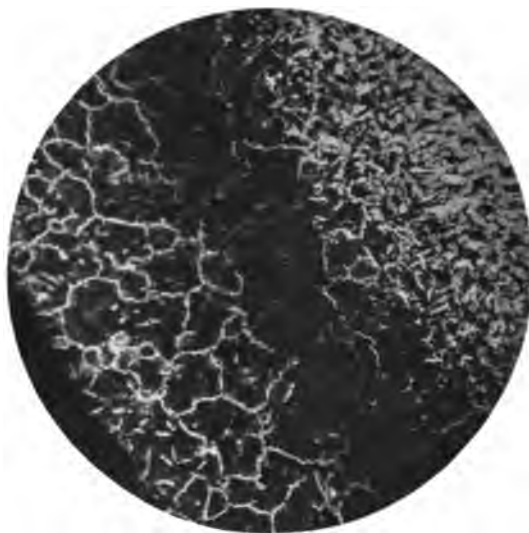


Fig. 295. — Steel. Case hardened. Magnified 20 diameters.

operation but, as already mentioned, carburization takes place more and more slowly as the carbon content increases. The maximum amount of carbon which iron can take up while in the solid state is probably not far from 2.50 per cent, this, however, requiring a protracted treatment at a very high temperature. While in the manufacture of blister steel considerably more than 1 per cent of carbon is frequently introduced into the wrought-iron bars, in carburizing finished steel articles it is seldom desired to produce a case containing more than 1 per cent of carbon near the outside, a superficial, carburized layer of eutectoid composition (0.85 per cent C) being generally considered to yield the best results. The length of time needed to produce the desired degree of carburization and desired depth of case must necessarily depend upon the nature of the metal, the kind of carburizing material used, and the temperature.

Distribution of the Carbon. — It will be apparent from the nature of the operation that in this carburizing of solid iron carbon travels slowly from the outside towards the center and that, therefore, the proportion of carbon absorbed must

decrease from outside to center, unless indeed the objects treated are very thin or the treatment so long and conducted at so high a temperature as to cause even the center to absorb the maximum amount of carbon. The decrease of carbon as one approaches the core of the object is well illustrated in Figures 295 and 296. A band of hyper-eutectoid steel characterized by the presence of free cementite is frequently noted (Fig. 295) followed by a band of eutectoid composition characterized by the absence of both free cementite and free ferrite and this in turn is followed by a band showing abrupt and rapid decrease of carbon characterized by an increasing amount of free ferrite.

In case-hardening operations the penetration of the carbon may be very slight indeed, not exceeding 0.5 mm., while it may measure as much as 5 mm. In the

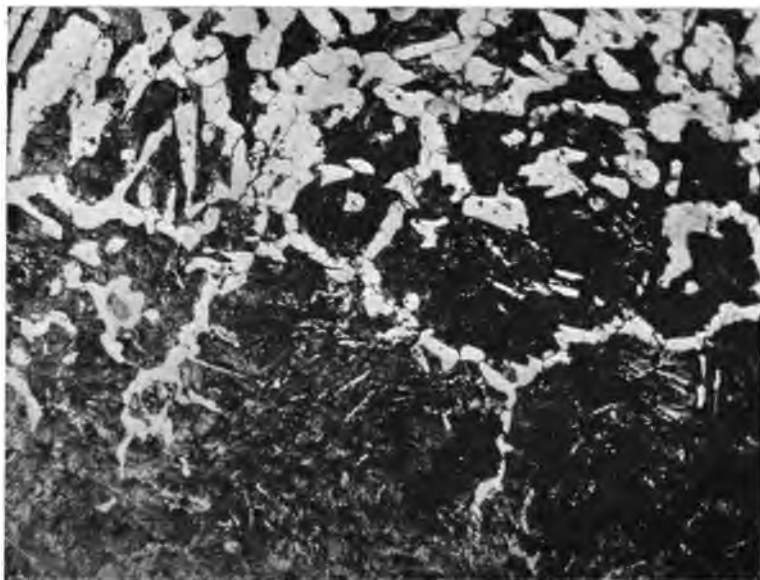


Fig. 296. — Steel. Case hardened. Magnified 100 diameters. (G. A. Reinhardt in the author's laboratory.)

majority of instances the penetration does not exceed 2 mm. This depth of penetration or thickness of case must be regulated according to requirements. It will depend upon temperature, time, composition of steel, and kind of carburizing material. Lake mentions 0.87 mm. per hour as an average speed of penetration. As already stated, it is not generally advisable to produce a case containing more than some 0.90 per cent carbon.

The production of a deep case, while at the same time keeping the carbon content of the outside of the case below 1 per cent, may be brought about by a rather long treatment at a relatively low temperature, namely, some 850 deg. C. Some results obtained by Guillet in regard to the influence of temperature and of time on the depth of penetration are shown graphically in Figure 297 as plotted by Bauer. The carburizing material used was not stated. The full line represents relative penetrations at 1000 deg. after different lengths of time, namely, one, two, four, and six hours, while

the broken line represents the depths of penetration resulting from heating for eight hours at different temperatures.

It will be obvious that the process of case hardening can be controlled by the microscopical examination of test pieces much more readily and accurately than by chemical analysis.

Carburizing Materials. — A great variety of carbonaceous materials is used for introducing carbon in iron and steel in the solid state. These substances may be solid, liquid, or gaseous. Solid materials are used more extensively than liquid or gaseous ones, the most important being charcoal (both wood and bone), charred leather, crushed bone, horn, mixtures of barium carbonate (40 per cent) and charcoal (60 per cent) or of salt (10 per cent) and charcoal (90 per cent), both recommended by Guillet, and for quick but very superficial hardening, powdered potassium cyanide and potassium ferro-cyanide or mixtures of potassium ferro-cyanide and potassium bichromate. A molten bath of potassium cyanide heated to 850 deg. and in which the steel articles are immersed produces quickly superficial but hard and

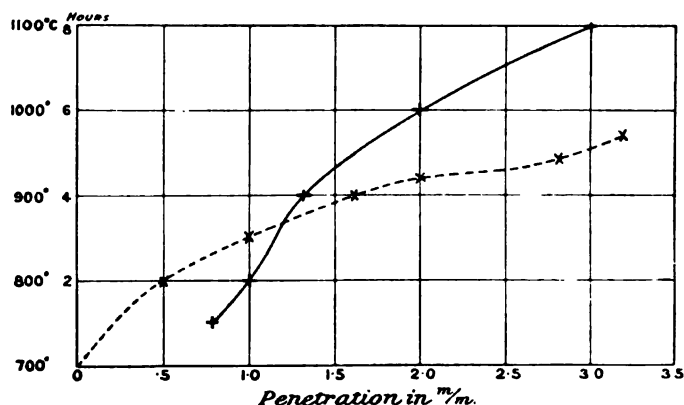


Fig. 297. — Temperature and time-penetration curve. (From Brearley's "The Heat Treatment of Tool Steel.")

even cases. The poisonous character of the escaping gases, however, is a serious objection to the use of this method. The carburizing of iron may also be performed at the proper temperature by means of gases such as illuminating or other coal or oil gases rich in carbon monoxide and in hydrocarbons. At the Krupp works in Germany gases are used for carburizing the faces of armor plates. Abbott states that out of 100,000 tons of carburizing material used in the United States in 1911, 85 per cent was granulated bone.

The relative merits of wood charcoal, charred leather, and a mixture of barium carbonate and of wood charcoal for carburizing are shown graphically in Figure 298, in which are plotted some results obtained by Shaw-Scott. While wood charcoal causes a slow carburization it is the best material and the one invariably employed for the production of very deep cases as, for instance, in making blister steel.

Giolitti surrounds the pieces to be case hardened with charcoal and then passes through the annealing box carbon monoxide or carbon dioxide gas, the latter upon coming in contact with red hot charcoal being converted into carbon monoxide

($\text{CO}_2 + \text{C} = 2\text{CO}$) which gas as later explained is the most active agent in carburizing. In Giolitti's opinion, however, CO when used alone generally fails to introduce enough carbon, but becomes much more effective when mixed with hydrocarbons or better still with finely divided solid carbon. Under these conditions the maximum concentration does not exceed 0.90 per cent carbon even after 8 hours at a *constant* temperature between 900 and 1100 deg. C. If the temperature be permitted to fluctuate, however, between 1000 and 1100 deg., the outer layers take up as much as 1.10 per cent carbon after an annealing of 3 hours' duration.

Many so-called secret mixtures are offered for sale as case-hardening substances for which extraordinary virtues are claimed, the usual statement being that by their use steel of ordinary or inferior quality may be converted into high grade metal com-

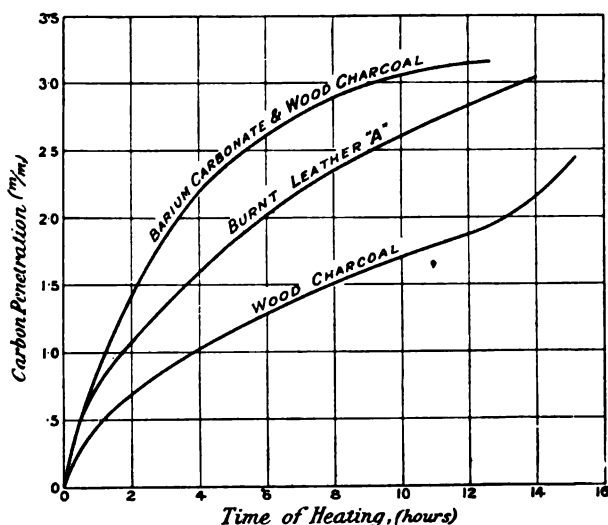


Fig. 298. — Time-penetration curve. (From Brearley's "The Heat Treatment of Tool Steel.")

parable to the best crucible tool steel. On investigation they are generally found to be chiefly mixtures of carbonaceous and cyanogen compounds possessing the well-known carburizing properties of those substances.

Case Hardening by Gas under Pressure. — Dr. F. C. Langenberg has conducted in the author's laboratory an extensive series of experiments dealing with the case hardening of American ingot iron with various gases under varying conditions of temperature, time, flow of gas, and pressure. Some of the most conclusive results obtained will be recorded.

Illuminating gas of the following composition:

Hydrogen	40.10 per cent	Oxygen	0.58 per cent
Methane	26.10 " "	Carbon Monoxide	11.38 " "
Nitrogen	14.04 " "	Heavy Hydrocarbons	4.95 " "
Carbon Dioxide	1.64 " "		

was passed through a tube furnace electrically heated and containing near the inlet end a plug of finely divided charcoal and, immediately following, small cylin-

ders of American ingot iron to be case hardened. The passing of the illuminating gas through the highly heated charcoal converted the CO_2 originally present into CO ($\text{CO}_2 + \text{C} = 2\text{CO}$) and may also have produced some changes in the hydrocarbons present. It is not probable that the hydrogen content was greatly, if at all, affected. Maintaining the flow of gas constant, at 5 liters per hour, the temperature likewise constant at 990 deg. C. for 3 hours, but varying the pressure from 0 to 115 lbs. per sq. in., a gradual increase in the carbon absorbed was observed as indicated both by increase of weight and depth of case. This is clearly shown by the curves of Figure 299. It will be noted that the increase is greatest

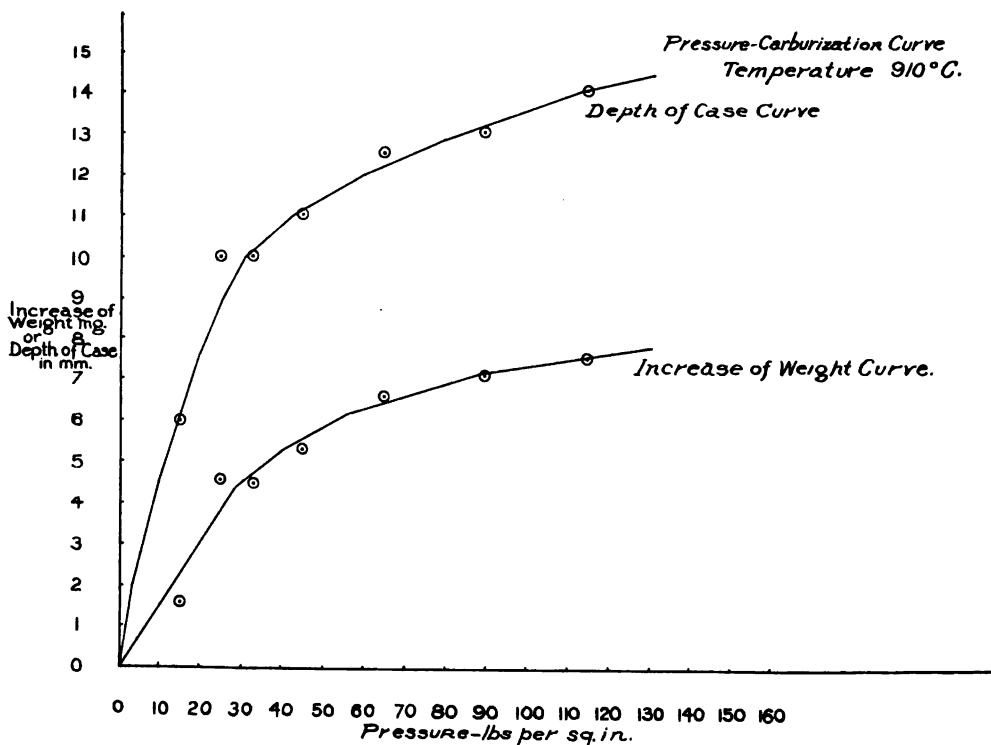


Fig. 299. — Case hardening by gas. Pressure-penetration curve. (F. C. Langenberg in the author's laboratory.)

as the pressure rises from 0 to some 40 lbs. per sq. in., both curves for higher pressure showing a tendency towards an horizontal deflection. This occurrence was found to be still more marked when the case-hardening operation was conducted at lower temperatures. In every instance, however, the bend in the curves occurred in the vicinity of 40 lbs. pressure. The photomicrographs (Figs. 300 to 302) clearly reveal the increasing depth of case resulting from increasing gas pressure, other conditions remaining unchanged. It should be observed that it is the hyper-eutectoid portion of the case which is chiefly affected, increasing in thickness with the pressure, while the width of the eutectoid band remains practically the same.

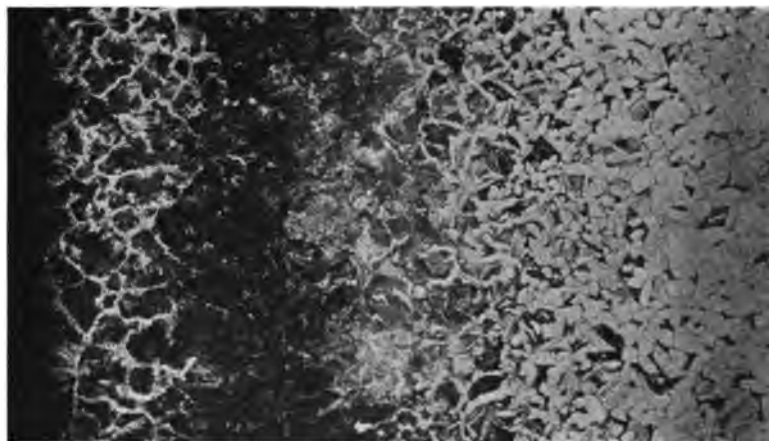


Fig. 300. — Pressure 26 lbs. per sq. in.

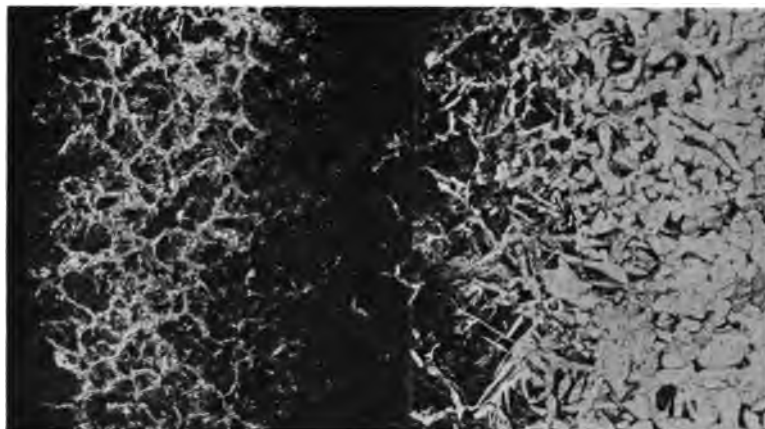


Fig. 301. — Pressure 45 lbs. per sq. in.

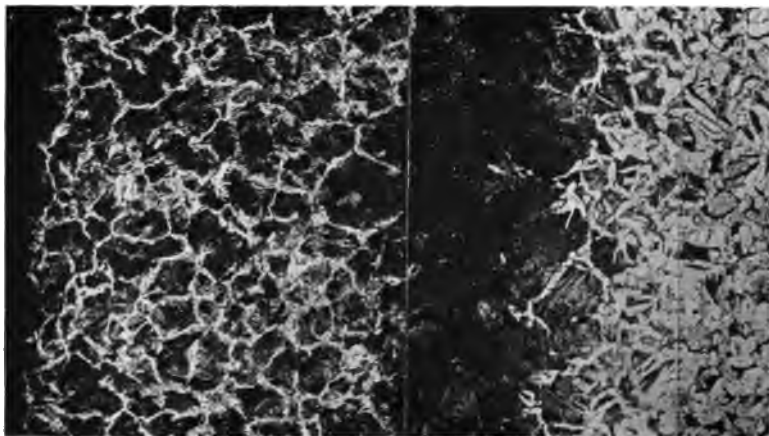


Fig. 302. — Pressure 75 lbs. per sq. in.

Case hardening by gas under increasing pressure. Temperature 990 deg. C. Time 3 hours. Flow of gas, 5 liters per hour. All photomicrographs are magnified 100 diameters. (F. C. Langenberg in the author's laboratory.)

Maintaining a constant atmospheric pressure, constant flow of gas (5 liters per hour), constant time (3 hours), but varying the temperature from 600 to 1000 deg. C., the curves of Figure 303 were obtained. They indicate the increasing amount of carbon taken up as estimated both by increasing weight and increasing depth of case. The following inferences appear justified: (1) at 700 deg. C. or at any lower temperature there was no absorption of carbon whatever, from which it may be concluded that α iron, under the prevailing experimental conditions, cannot dissolve carbon, (2) at 800 deg. C. there was a noticeable carbon absorption, hence the

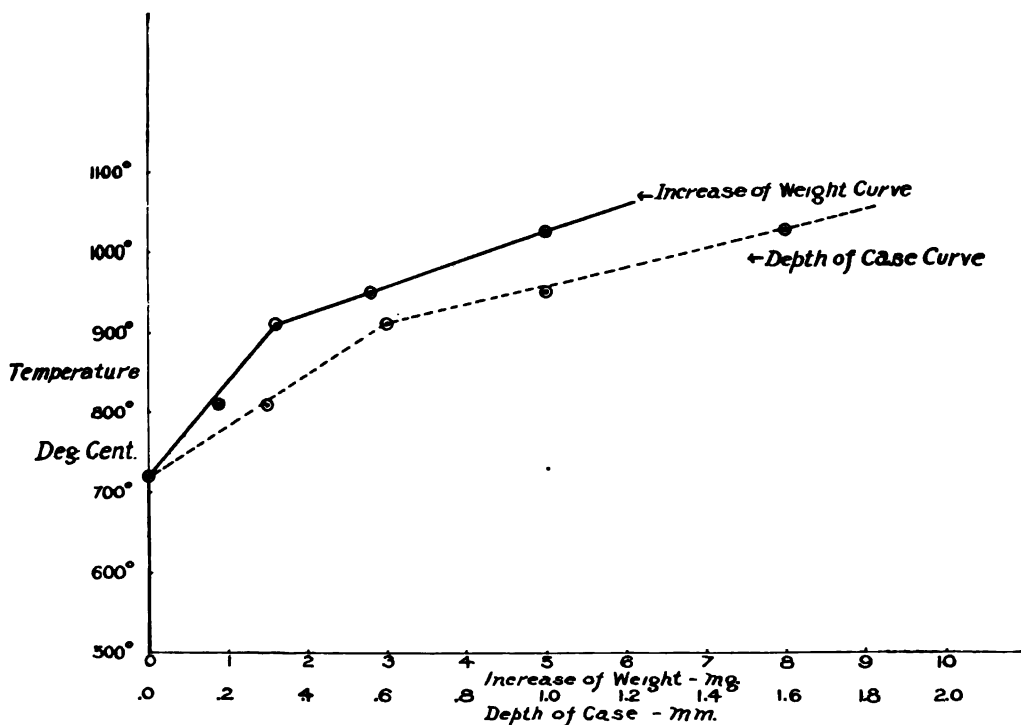


Fig. 303. — Case hardening by gas. Temperature-penetration curves. (F. C. Langenberg in the author's laboratory.)

power to dissolve carbon is acquired between 700 and 800 deg. C., that is during the range of temperature where β iron also is formed and it may be reasonably believed that the two occurrences are closely linked, (3) at 900 deg. there is a break in both curves indicative of a slower rate of increase, and this appears to be closely related to the formation of γ iron.

Figure 304 shows the structure of American ingot iron after the case-hardening operation just outlined conducted at 720 deg. C., while when performed at 810 deg. C. the structure of the same metal was as represented in Figure 305. There is no indication of the former having absorbed any carbon while the carburizing of the latter is very appreciable.

Mechanism of Cementation. — It was held for many years that in the cementation of iron solid carbon passed bodily from the packing material into the metal, fol-



Fig. 304. — American ingot iron case hardened by gas for 3 hours at 720 deg. C. Magnified 100 diameters. (F. C. Langenberg in the author's laboratory.)

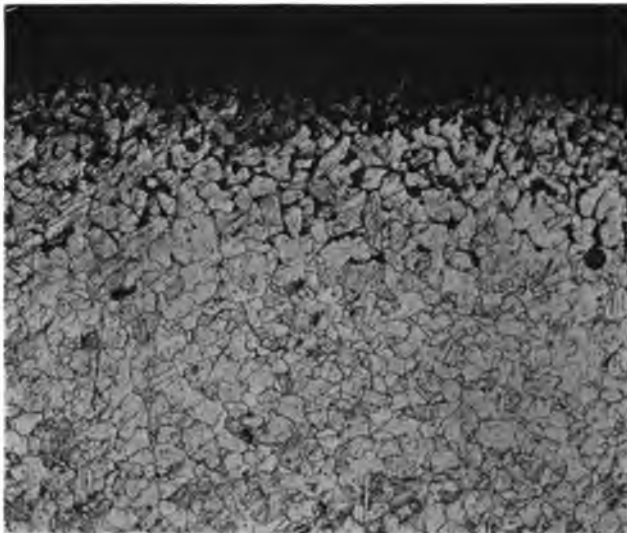


Fig. 305. — American ingot iron case hardened by gas for 3 hours at 810 deg. C. Magnified 100 diameters. (F. C. Langenberg in the author's laboratory.)

lowed by a slow migration towards the center. Recent investigations, however, have made it evident that the transfer of the carbon from the packing material to the metal is accomplished chiefly, if not altogether, by means of some gases liberated or formed during the annealing treatment. It has been shown quite conclusively, for instance, that if a piece of steel surrounded by pure carbon be heated in vacuum, thus precluding the formation of gases, it will not take up carbon, although one observer has noted that if decided pressure be applied some carbon will pass into the iron even in the absence of gases. Whether this be so or not it is apparently certain that the carbon must first be volatilized before becoming very active as a carburizing agent in the cementation and case-hardening treatments.

Carbon monoxide (CO) and volatilized cyanogen (CN) compounds are the gases which seem most effective. The carbon monoxide is derived from a partial combustion of the carbon of the cementing material by atmospheric oxygen while the cyanogen results from a combination of that carbon with atmospheric nitrogen or from the decomposition of cyanide compounds such, for instance, as potassium cyanide and ferro-cyanide. It may be assumed that the carbon monoxide once formed gives up its carbon to the iron according to the reaction,



the resulting Fe_3C or cementite being dissolved by the austenite very much as salt is dissolved in water and the CO_2 being again reduced to CO on coming in contact with fresh carbon ($\text{CO}_2 + \text{C} = 2\text{CO}$). The marked activity of cyanogen compounds compared to the slower action of charcoal have led some to believe that cyanogen gases are especially effective in carburizing iron. It should be noted, however, that while cyanide compounds produce a much quicker carburization they soon lose their carburizing power so that when deep cases are needed, as in the manufacture of blister bars, charcoal, acting chiefly through the production of carbon monoxide, is preferable.

Cooling from Carburizing Temperature. — It is generally desired that articles subjected to the case-hardening treatment should have a very hard surface. To produce this hardness the case-hardened articles should be quenched from above their critical range. The prolonged heating at a very high temperature to which these articles have been exposed, however, has developed a coarseness of structure both in the core and in the case which would be retained if they were, as they sometimes are, quenched from the carburizing temperature or after cooling to a somewhat lower temperature. It is obvious that in order to impart a fine structure both to the core and to the case the articles should be cooled and then subjected to suitable heat treatments.

Heat Treatment of Case-Hardened Articles. — In order to refine the structure of the core which has been coarsened by a long exposure to a high temperature the metal should be reheated slightly above the critical range of that core and since its carbon content seldom exceeds 0.15 per cent carbon a temperature of at least 900 deg. C. should be used. Guillet recommends 1000 to 1025 deg. The finer structure thus imparted to the core will then be retained most effectively by quenching the metal in water or oil. By such treatment, however, the case, although hardened, is still relatively coarse since its quenching was effected at a temperature considerably exceeding its critical range. In order to refine it while leaving the structure of the core undisturbed the article should now be reheated slightly above the critical range

of the case, that is, to some 775 or 825 deg. C., and then quenched in oil or water. By this double treatment we have hardened the case while conferring to it as well as to the core a fine structure.

It has been observed that the low carbon steel cores of case-hardened articles are frequently coarser than the same steel after like heat treatment conducted in the absence of carburizing material. This is generally ascribed to the action of hydrogen, most carburizing agents evolving some of that gas at the annealing temperature. This increased coarseness of the cores of case-hardened implements is an additional reason why their structure should be refined by suitable heat treatments.

Tempering Case-Hardened Steel. — The properties of quenched case-hardened steel may often be further improved by tempering, i.e. by reheating to some 200 to 400 deg. C. in order to toughen the case and remove strains while losing but little hardness.

CHAPTER XX

ALLOY STEELS

GENERAL CONSIDERATIONS

The steels so far considered in these chapters are the ordinary steels of commerce, at present often called "carbon" steels to distinguish them from the "special" or "alloy" steels of relatively recent origin but of rapidly growing importance. By special steels is meant those steels which owe their properties in a marked degree to the presence of one or more special elements whereas the properties of carbon steels depend chiefly, if not exclusively, for like treatment, upon the proportion of carbon present. Alloy steels containing but one special element are commonly called "ternary" steels, being considered to be made up of three constituents, namely iron, carbon, and the special element, while steels containing two special elements are called "quaternary" steels because of the presence of four constituents: iron, carbon, and the two special elements. These two classes of special steels will be considered separately.

Ternary Steels. — We are indebted to Guillet for a brilliantly conceived and vigorously developed theory of the ternary steels. Too rigorous an application of the theory, however, should not be insisted upon for there are some facts not yet satisfactorily explained by it. Its use, nevertheless, will be found an invaluable guide in directing researches dealing with the manufacture and the application of these steels.

Guillet's theory of the structure and properties of ternary steels may be briefly formulated by a few propositions. It is also represented graphically in Figure 306.

(1) On the introduction of a special element in carbon steel the latter remains at first pearlitic, but as the proportion of the special element increases, the carbon remaining constant, it becomes first martensitic and then austenitic (polyhedral), as shown graphically in Figure 306, and sometimes cementitic (carbide steel)¹ as later explained.

(2) By increasing the amount of carbon present in a special steel, the proportion of the special element being kept constant, it is generally converted from a pearlitic into a martensitic condition or, if already martensitic, into an austenitic condition.

(3) The greater the amount of carbon the smaller the proportion of the special element needed to cause a structural transformation, as for instance pearlite into martensite or martensite into austenite. This is indicated in Figure 306.

¹ Guillet uses the term "polyhedral" to designate an austenitic structure and "carbide" steel (*acier à carbure*) to indicate the presence of cementite (generally in special steels a double carbide of iron and the special element). It seems to the author that the terms austenitic and cementitic are preferable because they suggest unmistakably the nature of the constituents. Austenitic steels are not the only ones exhibiting a polyhedral structure; ferritic (low carbon) steels for instance are also polyhedral.

(4) The greater the amount of the special element the smaller the proportion of carbon needed to cause a structural transformation. This is also shown in Figure 306.

(5) No very sharp lines of demarcation are observed between the different types of structures mentioned in the preceding propositions, relatively wide ranges of composition existing, on the contrary, in which the steel may be partly pearlitic and partly martensitic or partly martensitic and partly austenitic, etc. These transition ranges are indicated by shaded areas in the diagram of Figure 306. Greater refinement in the construction of this diagram would undoubtedly lead to the introduction of a troostitic zone between the pearlite and martensite areas and possibly also of a sorbitic zone between pearlite and troostite.

To sum up, constituents may be formed during the *slow cooling* of many alloy steels which in carbon steels can only be produced by very rapid cooling through the

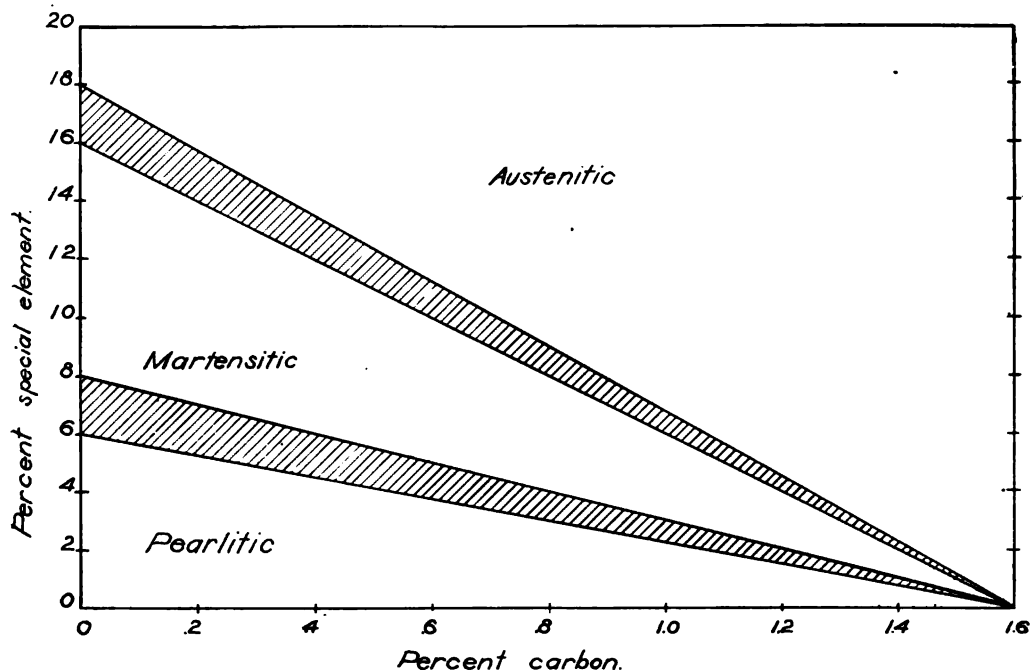


Fig. 306. — Constitutional diagram of alloy steels.

critical range. Carbon steels, moreover, even after very rapid cooling cannot be retained wholly in an austenitic condition while several special steels remain austenitic after slow cooling. It is evident from the above and from the diagram that in order to produce a certain structure, (1) the proportion of carbon may be kept constant while the proportion of the special element is increased until the desired structure is obtained, or (2) the proportion of the special element may be kept constant and the proportion of carbon increased, or (3) both the proportion of carbon and of the special element may be increased when the desired structure will be obtained more quickly.

The usefulness of Guillet's diagram is obvious. Should we desire, for instance, to know the kind of structure, and therefore the physical properties, of a steel containing 0.60 per cent carbon and 8 per cent of the special element, the diagram shows that such composition falls within the martensitic range. Likewise a steel contain-

ing 1 per cent carbon and 15 per cent of the special element would be austenitic according to the diagram. Or one may wish to know what proportion of the special element should be added to a carbon steel containing, say, 0.5 per cent carbon, to make it martensitic; the diagram shows that 7 per cent will be needed. Again, having an austenitic steel containing 10 per cent of the special element it may be desired to know the minimum amount of carbon that may be present without causing the steel to become martensitic; the diagram shows 0.80 per cent of carbon to be the smallest proportion of carbon permissible.

The construction of such diagrams requires the preparation of a number of alloys varying in their contents of carbon and of the special element, their microscopical examination and the plotting of their structure.

It is quite essential to know the rate of cooling adopted in the construction of the diagram, i.e. whether the samples were cooled in air or more slowly in the furnace, for it is evident that their structure may be deeply affected by thus varying the speed at which they cool. Some special steels, for instance, may be pearlitic when cooled very slowly in the furnace, martensitic when cooled in air, and austenitic after water quenching.

Influence of the Special Element upon the Location of the Critical Range. — The production of martensitic and austenitic structures on slow cooling is due to the fact that the special element lowers the position of the critical point to a temperature so low (1) as to permit only a partial transformation, namely, of austenite into martensite, the steel being too rigid to allow a more complete transformation, or (2) as to prevent even a slight transformation, the steel in that case remaining austenitic. This influence of the special element in lowering the position of the critical range is depicted in Figure 307 in which it is assumed that the proportion of carbon remains constant. It has been further arbitrarily assumed in this diagram that the critical point was progressively and uniformly lowered from 700 deg. C. to 0 deg., as the proportion of the special element increased from 0 to 6 per cent. From many observations it appears (1) that as long as the critical point remains above 300 deg. C. the steel becomes pearlitic on slow cooling, (2) that when the critical point is lowered below 300 deg. it becomes martensitic, the rigidity of the metal preventing further transformation, and (3) that when the critical point is lowered to atmospheric temperature or below it the metal remains untransformed, that is austenitic. These inferences are offered here because of their apparent usefulness and suggestiveness, but the author realizes that the lines indicating the relation between the position of the critical points and the corresponding structures cannot be sharply drawn, for they are likely to shift according to the nature of the special element, the rate of cooling, etc. Again, troostitic and possibly also sorbitic steel are likely to form between pearlite and martensite, that is, whenever the critical point is lowered, say below 400 or possibly below 500 deg.

To make the meaning of the diagram of Figure 307 clear let us consider three steels: I, II, and III, all containing 1 per cent of carbon, but respectively 1, 4.50, and 7 per cent of the special element. As steel I cools it undergoes its transformation at about 600 deg. At that temperature the metal is so plastic that the transformation of austenite into pearlite readily takes place; the steel becomes pearlitic. The critical point of steel II is slightly below 200 deg. At this temperature the transformation of austenite into martensite will take place, but the metal is now too rigid to permit further transformations; the steel remains martensitic. Steels which remain marten-

sitic after slow (air) cooling are said to be "self-hardening." In the case of steel III, since its critical point is lowered below atmospheric temperature it necessarily remains austenitic. Since austenitic special steels have their points of transformation situated below atmospheric temperature, it should be possible through cooling to a sufficiently low temperature, as for instance by immersion in liquid air, to cause at least their partial transformation, that is, they should become martensitic after such treatment and this indeed is precisely what happens in some cases. The transforma-

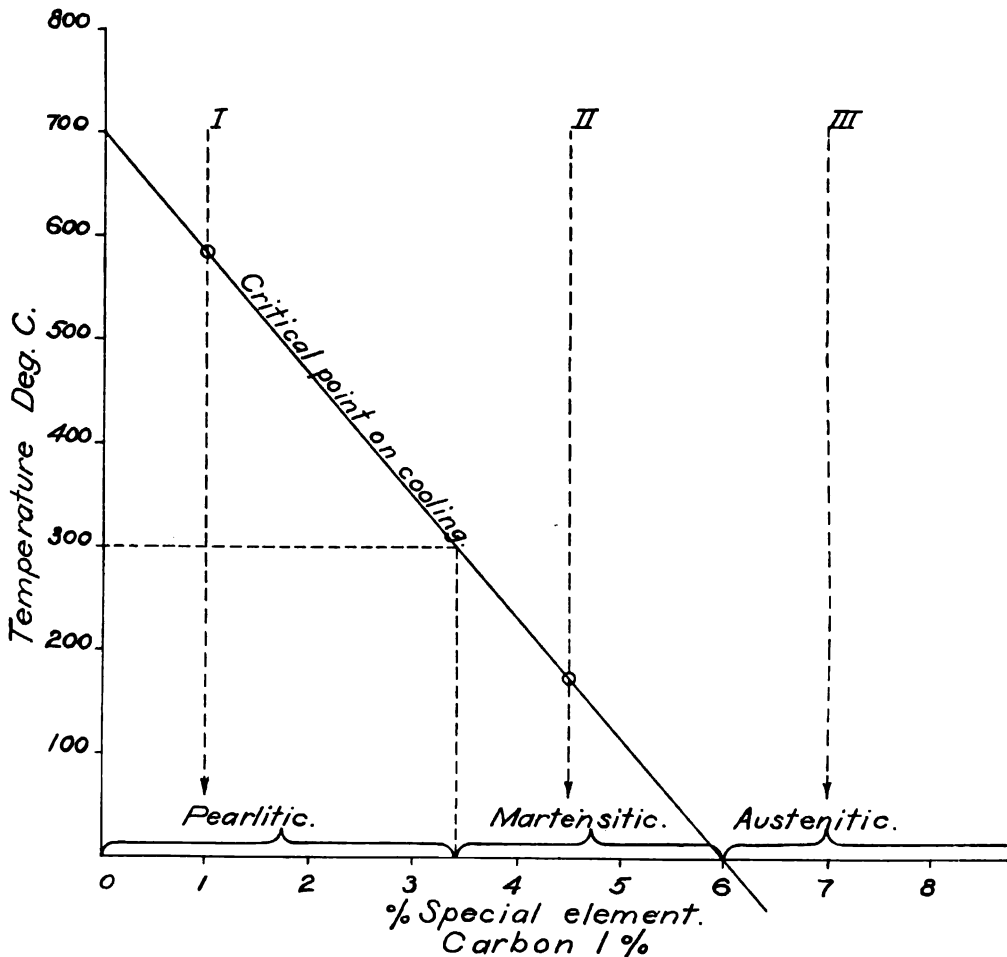


Fig. 307. — Influence of special element on the position of the critical point.

tion of austenite into martensite takes place with increased volume and the steel from non-magnetic becomes magnetic.

In the presence of a special element lowering the critical points the influence of carbon is cumulative, i.e. the greater the proportion of carbon the more marked the action of the special element. An attempt has been made in Figure 308 to show this graphically. The diagram indicates the position of the critical point corresponding to any combination of carbon content between 0.25 and 1.50 and of the special ele-

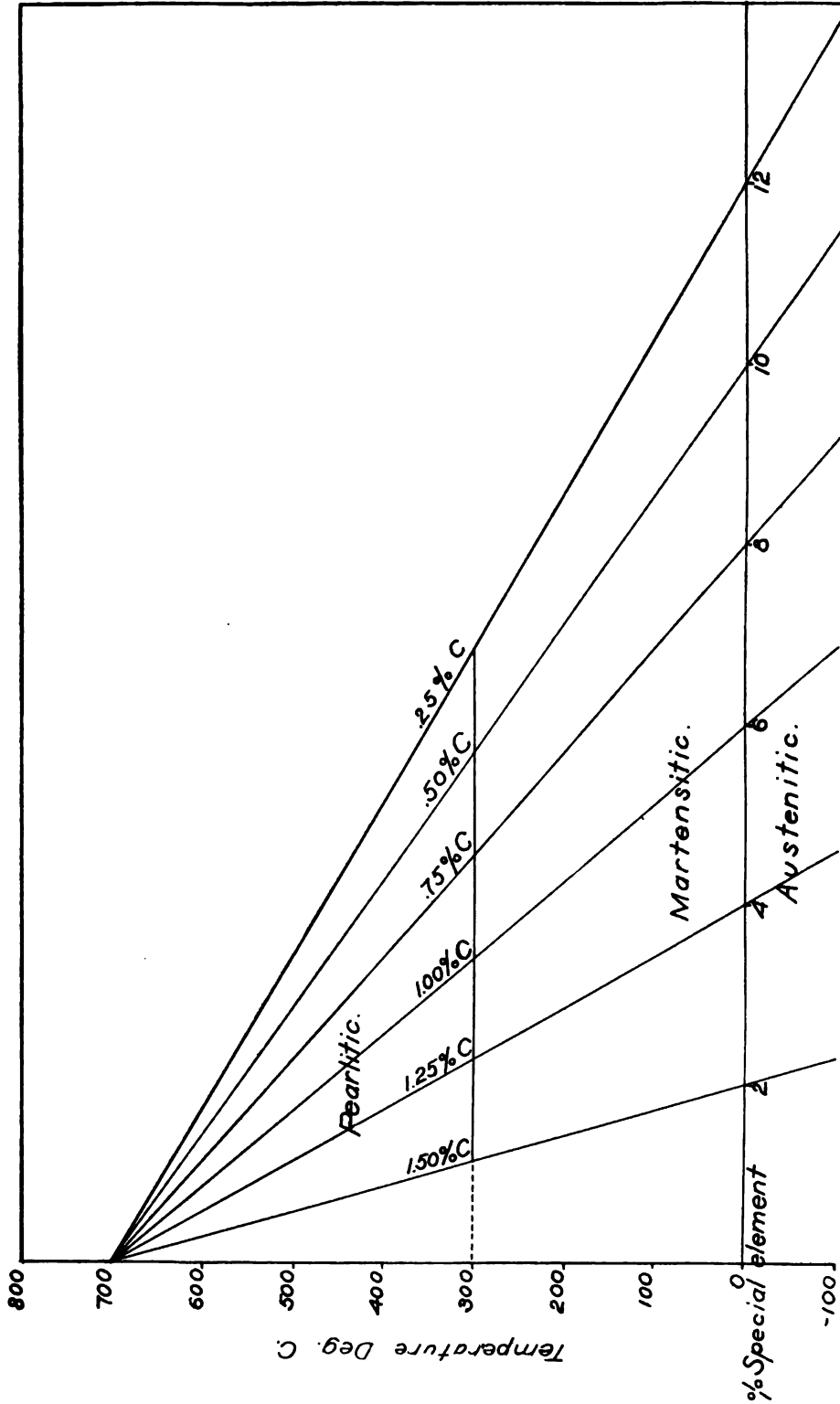


Fig. 308. — Influence of carbon and special element on the position of the critical point.

ment between 0 and 12 per cent. If the point is above 300 deg. we may assume that the steel is pearlitic, if below 300 that it is martensitic, if at or below atmospheric temperature that it is austenitic. In this illustration arbitrary values have been given to the combined influence of various proportions of carbon and of the special element upon the position of the critical points. The diagram shows, for instance, that while with 0.50 per cent carbon 10 per cent of the special element are required to lower the critical points to 0 deg. C., if the steel contains 1.25 per cent carbon, 4 per cent of the special element suffice. The production of pearlitic, martensitic, and austenitic structures according to the position of the critical point has also been indicated. A diagram of this kind may be even more useful than Guillet's for, while giving the same kind of information as his, it shows in addition (1) the relation between the composition of the special steel and the position of the critical point and (2) the influence of the position of the critical point upon the structure. Its construction calls for many determinations of the position of the critical point in steels of varying composition and for the microscopical examination of the corresponding structures. It is of course quite likely that as experimentally constructed it would consist of more or less smooth curves rather than of straight lines.

It will soon be shown that the influence of special elements in lowering the critical points varies greatly, from which it follows that some elements cause the production of martensitic and austenitic steels much more readily than others. Indeed some elements never cause a sufficient depression of the critical points to yield austenitic or even martensitic steels. A few elements even actually raise the location of the critical points in which case, of course, the steel always becomes pearlitic on slow cooling, regardless of its composition.¹

From the foregoing considerations it appears that according to their structural composition special steels may be divided into at least four classes, (1) pearlitic steels, (2) martensitic steels, (3) austenitic (polyhedral) steels, and (4) cementitic (Guillet's carbide) steels. These should now be further considered.

Pearlitic Steels. — The pearlitic steels, as we have seen, are those which generally contain but a relatively small amount of the special element, although in case of steel very low in carbon the proportion of the special element may be quite large. In these steels the special element may (1) be dissolved in the ferrite forming with it a solid solution, (2) be combined with carbon in cementite as a double carbide of iron and the special element, or (3) be partly dissolved in ferrite and partly combined with carbon.

According to Guillet nickel and silicon, for instance, are entirely dissolved in ferrite, while manganese, chromium, tungsten, vanadium, and molybdenum are partly held in solution by ferrite and partly present in cementite as double carbides. Such terms as nickel-ferrite, silico-ferrite, mangano-ferrite, etc., have been suggested to designate ferrite holding in solution large proportions of nickel, silicon, manganese, etc., respectively.

The structure of pearlitic alloy steels is generally quite similar to that of pearlitic carbon steels, although the pearlite particles of special steels frequently are more angular than those of carbon steel, often exhibiting many straight sides and sharp corners, whereas the pearlite particles of carbon steel are more rounded. The lami-

¹ It has been claimed by some that in certain alloy steels exhibiting the two points A_1 and A_2 while A_2 always remains at the same temperature, A_1 may be raised above A_2 through suitable regulation of composition and heat treatment.

nation of pearlite is also often more minute in special steels while for same carbon content it often appears to occupy a larger bulk. From their similarity of structure, it might reasonably be inferred that pearlitic special steels should not differ much in physical properties from ordinary carbon steels. As a matter of fact, however, pearlitic special steels are often greatly superior to carbon steels generally because they possess in a much greater degree that desirable combination of properties, strength, or rather high elastic limit, and ductility. They are also frequently harder for like ductility, and therefore better adapted to resist wear. Finally their ability to resist shocks is often markedly superior to that of carbon steels. Their uses make for greater efficiency and their greater strength permits an often welcome reduction in bulk and weight of certain parts of machinery. This greater strength and stiffness of special pearlitic steels may be due to the special element dissolving, in part at least, in the ferrite thereby increasing its strength, elastic limit, and hardness, a stronger and harder ferrite resulting in turn in a stronger and harder pearlite. The superior physical qualities of these steels may also be due, at least partly, to a finer, closer ferrite-cementite aggregate.

The critical points of special pearlitic steels generally occur at temperatures somewhat lower than those at which the critical points of carbon steel are located, this being in accord with the usual influence of special elements upon these points as already explained.

Martensitic Steels. — For the same carbon content martensitic steel contains necessarily more of the special element than pearlitic steels, while for a given proportion of the special element they must contain more carbon; they generally contain both more carbon and more of the special element than pearlitic steels. As already stated the influence of some special elements in lowering the critical points is not sufficiently pronounced to result in the formation of martensite on slow cooling. Indeed some elements raise the position of the critical points in which case pearlitic steel must necessarily always be formed on slow cooling.

The properties of martensitic special steels are not unlike the properties of martensitic carbon steels, that is of hardened carbon steel. These steels are hard and brittle and unforgeable in the cold. Their uses are very limited, chiefly because of their brittleness and of the difficulty of machining them. While resembling hardened carbon steels they are quite stable above atmospheric temperature, being little affected by tempering, i.e. by reheating to 200 or 300 deg. C. This property suggests one important application at least of martensitic special steels later to be considered, namely, their use for the manufacture of cutting tools, their greater stability permitting the tools to be heated to a higher temperature, i.e. the cutting being performed at greater speed without breaking down through excessive tempering.

The martensite of special steels probably is, like the martensite of carbon steels, chiefly a solid solution in beta iron of the carbide Fe_3C or more often of a double carbide of iron and of the special element, the magnetism of the metal being due to the presence of some alpha iron.

Austenitic (Polyhedral) Steels. — For a given carbon content austenitic steels necessarily contain more of the special element than martensitic steels, while for a given proportion of the special element they are necessarily more highly carburized. Austenitic steels generally contain both more carbon and more of the special element than martensitic steels. Their properties are as might be expected similar to those of austenitic carbon steels, that is, of high carbon steels cooled extremely quickly from

a very high temperature. Austenitic steels are moderately tenacious but very ductile; they have a low elastic limit but possess a remarkable power of resisting wear by abrasion as well as rupture by shocks. The mineralogical hardness, however, is generally inferior to that of martensitic steels.

Unlike quenched austenitic carbon steel these special steels are stable at all temperatures below their point of solidification and are not therefore greatly affected by heat treatment unless of a protracted nature. They should be free, however, from separated carbides. If not they should be heated to a high temperature so as to cause the solution of these carbides, and then quenched to prevent their separating again.

The austenite of special steels undoubtedly consists of a solid solution in gamma iron of carbon and of the special element, probably of a double carbide. Because of the absence of alpha iron austenitic steels are non-magnetic.

Austenitic special steels find useful application for parts of machinery and the like subjected to very severe wear by abrasion and to shocks. Their low elastic limit and the difficulty of machining them are the chief reasons preventing their wider use.

Cementitic (Carbide) Steels. — Some special elements on being introduced in increasing proportions fail to convert the metal into austenite, free particles of a double carbide of iron and the special element being formed instead and embedded in a martensitic, troostitic, sorbitic, or pearlitic matrix. Guillet calls these "carbide" steels. Such elements as chromium, tungsten, molybdenum, and vanadium when present in sufficient quantity produce cementitic steels. The most valuable property of these steels is their power, when the carbides are embedded or rather dissolved in a martensitic or austenitic matrix, of retaining their hardness when heated to such temperature as would readily cause the softening of hardened carbon steel, thus permitting their use in the shape of tools at such speed as to cause their cutting edges to become visibly hot. This phenomenon will be further explained when describing self-hardening and high speed steels.

Treatments of Special Steels. — Special steels are subjected to the same treatments as carbon steels, i.e. to hot and cold working, annealing, hardening, and tempering, and to case hardening. Since the special elements, however, often have a marked influence on the position of the critical points it is obvious that the temperatures indicated as the most suitable ones for the annealing and hardening of carbon steels may not be satisfactory in the case of special steels. The position of the critical points should in every case be determined and the heat treatments conducted accordingly. Greater care is also frequently needed in the forging of special steels, many of them not being quite as malleable as carbon steels. Finally some of the special elements promote the absorption of carbon by iron below its solidification-point while others oppose it and these influences must be considered in case hardening special steels. The treatment of special steels will be considered further in the next chapter in connection with the description of some of the most important commercial types.

Treatment of Pearlitic Steels. — Pearlitic special steels may, like carbon steels, be subjected to annealing, hardening, tempering, and case hardening. Their critical points, however, being generally lower, the proper temperatures for these operations are likewise lower. They should be determined for each steel. According to Guillet, however, the steel should be heated quite a little above its critical range because in the case of the pearlite of special steels its transformation into a solid solution does not take place as readily. The steel should then be cooled to near its critical range before quenching. Guillet writes that pearlitic special steels may be divided into

(1) those that are not very sensitive to annealing, namely nickel and silicon steels, and (2) those that are very sensitive to annealing, namely, manganese, chrome, vanadium, tungsten, and molybdenum steels. It should be noted that in the first group the special elements are supposed to be entirely dissolved in the iron, while in the second group they are partly dissolved and partly present as carbides. The case hardening of pearlitic special steels may result in the production of martensitic or even austenitic cases without the necessity of rapid cooling from above the critical range. This will be readily understood by referring to Figure 306 where it will be seen that by keeping the proportion of the special element constant and increasing the carbon the steel may be converted from a pearlitic to a martensitic and even to an austenitic condition. The nearer the steel to the boundary between the pearlitic and martensitic zones the more readily, of course, will it become martensitic on case hardening because the smaller the amount of carbon needed to produce that transformation. This possibility of producing steel objects with a pearlitic soft core and a hard martensitic shell without quenching from a high temperature and therefore without exposing the objects to the dangers of the quenching bath does not seem to have received the attention it deserves for it suggests important practical applications. And likewise the production of a soft pearlitic core surrounded by a hard martensitic steel, itself surrounded by a tough austenitic steel. It points at least to the manufacture of pearlitic steel objects which can be readily machined, etc., and as a last treatment made austenitic to a certain depth, being in this way greatly superior to the austenitic steels at present used, which being cast in an austenitic condition can be machined only with very great difficulty.

Treatment of Martensitic Steels. — Unlike martensitic carbon steels martensitic special steels being quite stable below the critical range of the metal are not readily affected by tempering treatments. It should be borne in mind, however, that some special steels which are martensitic after air cooling may become pearlitic, in part at least, after very slow cooling in the furnace and austenitic or martensitic-austenitic after quenching in water. By selecting a special steel of suitable composition, for instance, and allowing it to cool in a furnace it becomes pearlitic and can in consequence be machined; after machining the finished object may be made martensitic by cooling in air, doing away with the necessity of the quenching bath and its inherent evils. It is evident that for this purpose the composition of the steel should be near the boundary line between the pearlitic and martensitic zones. The author believes that the practical possibilities of this procedure have been overlooked. When working near the pearlitic-martensitic boundary line the formation of troostite is of course always likely.

Treatment of Austenitic Steels. — Austenitic special steels are stable theoretically at least at all temperatures and should not, therefore, be affected by heat treatment of any kind. Some special steels, however, may require air cooling to be truly austenitic, in which case very slow cooling in the furnace may result in the production of some martensite or troostite and even of some pearlite, accompanied by the reappearance of magnetism. It also frequently happens that during the relatively slow cooling of austenitic steels some free cementite may be formed, consisting generally of a double carbide of iron and the special element, this setting free of cementite being generally accompanied by a decided decrease of strength and ductility. In order to cause the reabsorption of the separated carbide heating to a high temperature (1000 deg. C. or higher) is generally required followed by rapid cooling in

water or oil so as to prevent its separating again on cooling. This treatment is sometimes called "water toughening."

Treatment of Cementitic Steels. — Cementitic steels contain many particles of cementite or double carbide embedded in a matrix which may be austenitic, martensitic, troostitic, sorbitic, or pearlitic according to the rate of cooling. It is often desirable to cause the disappearance in part at least of these particles while producing a finely martensitic or austenitic structure, and for this purpose heating to a high temperature (1000 deg. C. or more) followed by relatively quick cooling is necessary. Cooling in air is often sufficiently rapid to retain the carbide in solution, as for instance in the case of the high speed steels soon to be described.

Quaternary Steels. — Quaternary steels like ternary steels may be pearlitic, martensitic, austenitic, or cementitic as well as sorbitic and troostitic. If the two special elements are present in small quantities the steels remain pearlitic. If they contain one or two cementite forming elements such as chromium, tungsten, molybdenum, etc., they are likely to be cementitic, that is, to contain many particles of a double or triple carbide. These should generally be made to dissolve in the matrix by heating to a high temperature followed by rapid cooling when a finely martensitic or austenitic structure, quite free from cementite, may be produced as in the treatment of high speed steel. If the quaternary steels contain considerable proportions of two special elements capable of forming solid solutions with iron, as for instance nickel and manganese, they are frequently martensitic or austenitic. A large proportion of an element which is partly dissolved in ferrite and partly present in cementite as a double carbide, manganese, for instance, may result in the occurrence of cementite particles embedded in an austenitic matrix.

CHAPTER XXI

ALLOY STEELS

CONSTITUTION, PROPERTIES, TREATMENT, AND USES OF MOST IMPORTANT TYPES

The present chapter is devoted to a brief consideration of the composition, structure, properties, treatments, and uses of those special steels which have been found to be of commercial value, namely, nickel, manganese, tungsten, chromium, vanadium,

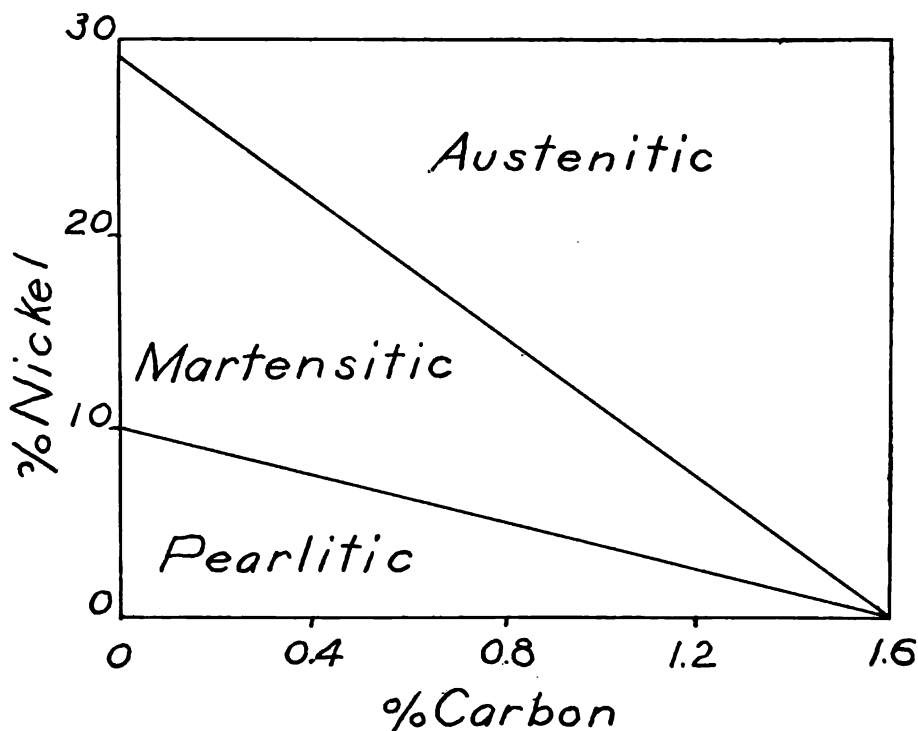


Fig. 309. — Nickel steel. Constitutional diagram. (Guillet.)

silicon, molybdenum, chrome-nickel, chrome-vanadium, chrome-tungsten, and chrome-molybdenum steels.

Nickel Steel. — Nickel apparently dissolves in iron in all proportions. The constitutional diagram of nickel steel is illustrated in Figure 309 after Guillet. In view of the explanation of such diagrams given in the preceding chapter it will be readily understood. It shows that as the carbon increases from 0 to 1.60 per cent and the

nickel from 0 to 30 per cent the metal which at first remains pearlitic becomes martensitic, and finally austenitic. The nickel steels of greatest commercial importance seldom containing more than 5 per cent nickel and 1 per cent carbon are pearlitic. This influence of nickel in preventing partly or wholly the transformation of austenite into pearlite is due to its lowering the critical point of the steel as fully explained in the last chapter and as illustrated graphically in Figure 310 in the case of iron-nickel alloys containing small proportions of carbon. It should be remembered that the presence of larger quantities of carbon would intensify the influence of nickel, i.e. would cause the critical points to be further depressed. The diagram shows that as the nickel increases from 0 to some 25 per cent both transformations, AB on cooling and $A'B'$ on heating, are depressed, the former, however, much more quickly than the latter, resulting in a rapidly increasing gap between the two transformations. In

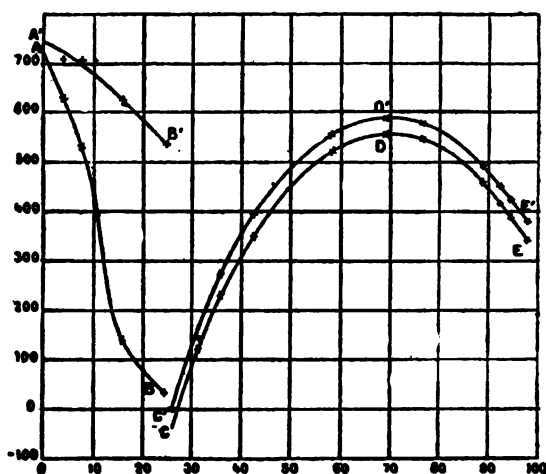


Fig. 310. — Influence of nickel on the critical points of iron. (Osmond.)

other words, nickel up to 25 per cent greatly increases the hysteresis. Taking a steel, for instance, with 10 per cent nickel cooling from a high temperature, it remains non-magnetic until a temperature of some 400 deg. C. is reached when it undergoes the magnetic and other transformations. On reheating this magnetic steel, however, it does not again lose its magnetism until a temperature of some 675 deg. is attained. Between 400 and 675 deg. this nickel steel will be magnetic, therefore, in case its last transformation resulted from cooling below 400 deg. and it will be non-magnetic if it resulted from heating above 675 degrees. When this hysteresis gap between the transformation is considerable the alloys are said to be irreversible, meaning by that expression that the reverse transformation cannot be produced at or near the same temperature. Nickel steels containing between 5 and 25 per cent nickel are therefore often spoken of as irreversible alloys. It should be noted, that when the nickel content does not exceed some 3 per cent the alloys are really reversible, that is, the gap between the critical transformations on heating and cooling is not excessive. According to Osmond, for instance, with 3.82 per cent nickel the critical point on heating occurs at 710 deg. and on cooling at 628 degrees. A gap of 100 deg. might be

arbitrarily selected as a line of demarcation between reversible and irreversible alloys. Returning to Figure 310 it will be seen that as the nickel content increases above 25 per cent the transformations become abruptly reversible (the gap between them not exceeding 50 deg.), that their position is now gradually lifted, reaching a maximum for about 70 per cent nickel, and that it is then again lowered. Iron-nickel alloys containing more than 25 per cent nickel are therefore reversible.

The diagram also shows that with some 25 per cent nickel the transformation is lowered below atmospheric temperature which means that the metal on cooling from above B' remains non-magnetic at atmospheric temperature and that its iron, therefore, is in the gamma condition and its structure austenitic.

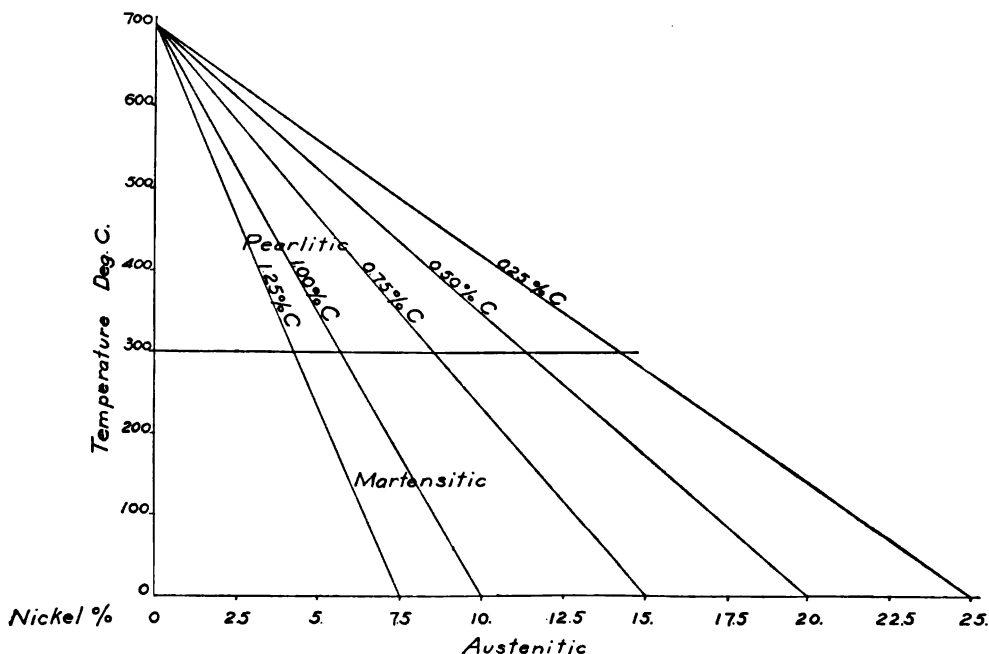


Fig. 311. — Influence of nickel and carbon on the position of the critical point Ar_1 and corresponding types of structure.

An attempt has been made in Figure 311 to construct a diagram indicating the relation existing between carbon content, nickel content, position of the critical points on cooling, and corresponding types of structures as explained in Chapter XX.

As already stated the pearlitic nickel steels are those most widely used. In the majority of cases the nickel content does not exceed 3.50 per cent while the carbon content is seldom over 0.50 per cent. These steels compared with carbon steels of equal ductility have a considerably higher strength and especially higher elastic limit, while compared with carbon steels of like elastic limit they have much greater ductility. To explain this in another way, the introduction of some 3.50 per cent nickel in a 0.50 per cent carbon steel, for instance, raises its elastic limit very considerably while decreasing its ductility but slightly. Pearlitic nickel steels are also somewhat harder than carbon steels of like properties, hence better able to resist wear. When properly heat treated their ability to resist shocks is likewise greater.

The structure of pearlitic nickel steel is shown in Figure 312. On comparing it with that of carbon steel of like carbon content it will be noted that the pearlite particles are somewhat sharper and more angular and the ferrite grains smaller. When examined under high magnification the nickel pearlite is seldom found as distinctly laminated as ordinary pearlite.

The hardening and annealing of nickel steels should be conducted at lower temperatures than the hardening and annealing of ordinary steels of similar carbon content since their critical points occur at lower temperatures. From the evidences at hand it would seem as if between 0 and 5 per cent nickel, and in the case of low carbon steels, each 1 per cent of nickel lowered the A_{r1} point some 20 deg. C. and the



Fig. 312. — Nickel steel. Carbon about 0.30 per cent.
Nickel about 3 per cent. Magnified 100 diameters.
(G. A. Reinhardt in the author's laboratory.)

A_{c1} point some 10 degrees. In the nickel pearlitic steels of commerce, therefore, the points A_{r1} and A_{c1} should occur at or near the temperatures indicated in the following table according to their percentage of nickel.

% Ni	A_{c1}	A_{r1}
0	750	700
0.50	745	690
1.00	740	680
1.50	735	670
2.00	730	660
2.50	725	650
3.00	720	640
3.50	715	630
4.00	710	620
4.50	705	610
5.00	700	600

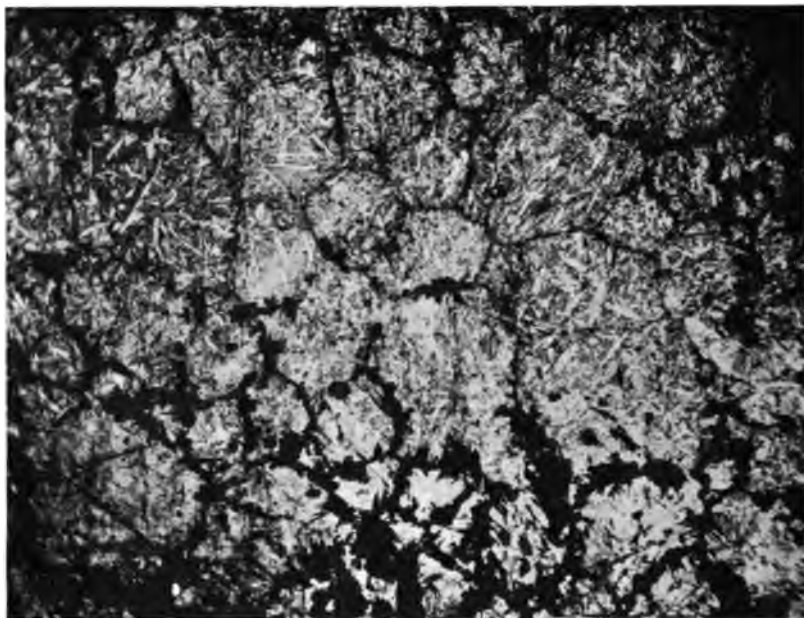


Fig. 313. — Nickel steel. Nickel 3.44 per cent. Carbon 0.176 per cent. Case hardened and air cooled. Magnified 100 diameters. (G. A. Reinhardt in the author's laboratory.)

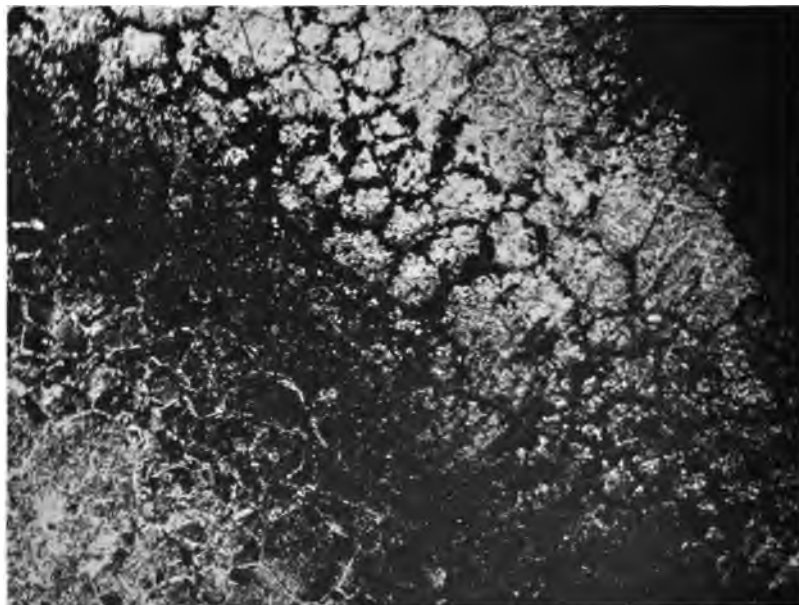


Fig. 314. — Same steel as in Figure 313. Same treatment. Magnified 50 diameters. (G. A. Reinhardt in the author's laboratory.)



Fig. 315. — Nickel steel. Nickel 4.86 per cent. Carbon 0.115 per cent. Case hardened and air cooled. Magnified 100 diameters. (G. A. Reinhardt in the author's laboratory.)



Fig. 316. — Same steel as in Figure 315. Same treatment. Magnified 300 diameters. (G. A. Reinhardt in the author's laboratory.)

While nickel retards the carburization of iron by case hardening, the cores of nickel steel articles are not coarsened by the high temperature of the carburizing operation to the same extent as carbon steel cores, so that one treatment is often sufficient, namely, reheating to and quenching from a temperature slightly superior to the critical range of the case, that is, to some 700 to 750 deg. in the presence of some 3 or 3.5 per cent nickel. Higher nickel contents call for lower quenching temperatures.

The case hardening of nickel steels offers the possibility already alluded to of producing a martensitic case without quenching. Nickel steel, for instance, containing not over 0.25 per cent carbon and some 3.50 or more per cent nickel can readily be made martensitic near the outside by case hardening followed by air cooling as

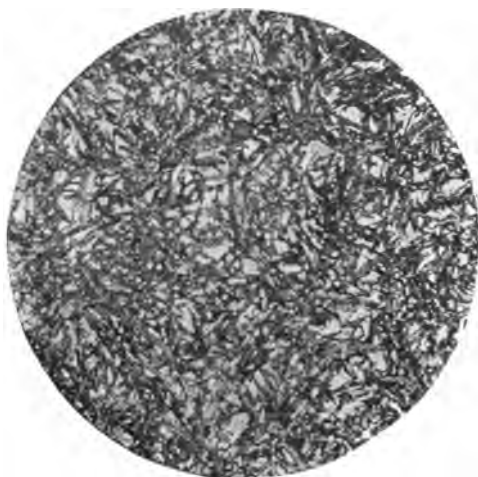


Fig. 317. — Nickel steel. Cast. Nickel 10 per cent. Carbon 0.80 per cent. Magnified 300 diameters. (Guillet.)



Fig. 318. — Nickel steel. Nickel 25 per cent. Carbon 0.80 per cent. Magnified 300 diameters. (Osmond.)

shown in Figures 313 and 314. The martensitic grains owe their polyhedral form to the original austenitic grains from which they are derived. The thickness of the martensitic case is about 0.5 mm. The occurrence of troostite should be noted. Under lower magnification (Fig. 314) a solid troostite band is seen to separate the martensitic and the sorbito-pearlitic portions. With a little more carbon and nickel martensite-austenitic cases may be produced as shown in Figures 315 and 316.

Nickel steels that are martensitic as cast are not utilized because like all martensitic steels they are hard, brittle, and cannot be machined. Their case hardening should result in the formation of ductile, austenitic cases. Nickel steels which are martensitic after air cooling may be troostitic, sorbitic, or even pearlitic after very slow cooling in the furnace, while they may become austenitic on water quenching. The structure of martensitic nickel steel is shown in Figure 317.

Austenitic nickel steels are not widely used, the high carbon, high manganese steels being preferred when an austenitic steel is desired, in part at least because of their lower cost. Like all austenitic steels they are non-magnetic, ductile, very difficult to machine, and have a low elastic limit. Their structure is polyhedral (see

Fig. 318). Some types of austenitic nickel steels have, however, found interesting applications based chiefly on the marked influence of nickel on the dilatation of the metal. With 36 per cent nickel, for instance, the dilatation is nearly nil and the resulting alloy, discovered by Guillaume, and called by him "invar" is used successfully for the construction of clocks and other instruments of precision. With some 46 per cent of nickel and 0.15 per cent carbon the coefficient of dilatation is nearly the same as that of glass and alloys of that composition called "platinite" are used in place of platinum for the construction of incandescent electric lamps. Austenitic nickel steel may be made martensitic and thereby regain its magnetism by immersion in liquid air. The increase of volume which accompanies this transformation produces a swelling of the polished surface which because of the resulting relief effect renders the structure of the metal apparent without etching, as shown in Figure 319.



Fig. 319. — Nickel steel. Nickel 15 per cent. Carbon 0.80 per cent. Cooled in liquid air (-180 deg. C.). Not etched. Magnified 300 diameters. (Guillet.)

Manganese Steel. — Manganese, when alloyed with iron and carbon in large proportion, is partly dissolved in the iron and partly present as a double carbide of iron and manganese. From this behavior of manganese the structural types formed by increasing both carbon and manganese may be anticipated. The steel should at first remain pearlitic and then become in succession martensitic and austenitic. With much manganese and carbon, however, the separation of carbide is to be expected. The constitutional diagram of manganese steels is shown in Figure 320 after Guillet, while a critical point structural diagram has been constructed tentatively in Figure 321. By comparing the constitutional diagram of manganese steel with that of nickel steel it will be noted that manganese is, roughly stated, twice as effective as nickel in producing a certain type of structure, as for instance in converting pearlitic into martensitic steel.

Manganese is present in appreciable quantities in all ordinary carbon steels but unless the latter contain considerably more than 1 per cent of that element they are not regarded as manganese steels. With carbon not exceeding 0.80 per cent and

manganese not exceeding some 3 per cent the steels remain pearlitic and, therefore, not unlike the pearlitic nickel steels so widely used. Manganese pearlitic steels, however, are practically ignored by steel manufacturers and users apparently (1) because of the wide-spread belief that such steels are brittle and (2) because of the difficulty of manufacturing low carbon manganese steels. The belief in the brittleness of pearlitic manganese steels is founded on Hadfield's statement that between 2 and 6 per cent of manganese the steels are hopelessly brittle. On closer examination, however, it would seem as if this statement was true only in the case of rather high carbon steels cooled relatively quickly. Evidences have since been offered,

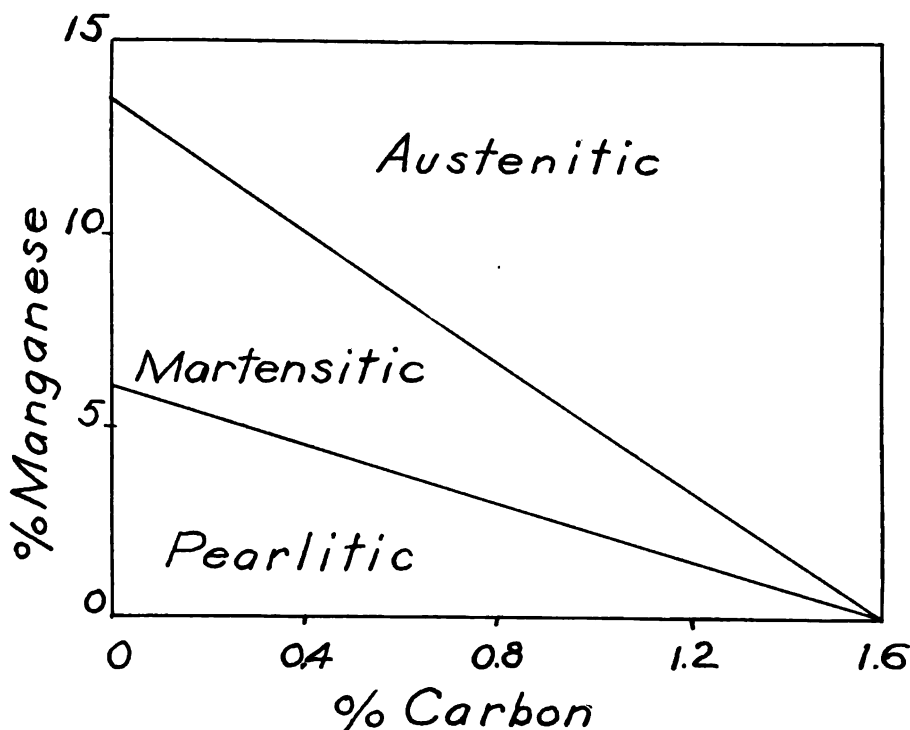


Fig. 320. — Manganese steel. Constitutional diagram. (Guillet.)

notably by Guillet, showing that *low carbon pearlitic manganese steel slowly cooled* is not brittle.¹ These steels have been difficult to manufacture because of the necessity of using ferro-manganese from the blast furnace and therefore high in carbon, thereby introducing much carbon in the steel. At present, however, nearly carbonless ferro-manganese is produced in electric furnaces and also by the thermit process. It is also claimed that low carbon manganese steels can be successfully produced in the electric furnace under suitable oxidizing conditions and at high temperature when carbon may be oxidized in preference to manganese. If the physical properties of low carbon pearlitic manganese steel are at all comparable to those of pearlitic nickel steel and if manganese steel can be manufactured more cheaply than nickel steel of

¹ Arnold reports that steel containing less than 0.10 per cent carbon and 5.50 per cent manganese has a tensile strength of some 145,000 pounds per square inch and an elongation of 28.50 per cent.

like properties the manufacture and testing of low carbon manganese steel should receive more attention. The possibility of producing by case hardening articles having pearlitic cores and austenitic cases also deserves some consideration. Martensitic manganese steels are not utilized because of the hardness and brittleness which they share with all martensitic steels. Those manganese steels whose composition is near the boundary line between the pearlitic and martensitic regions while martensitic after air cooling may be troostitic or even pearlitic after very slow cooling while they may become austenitic on quenching.

Austenitic manganese steel is of considerable industrial importance. It is often called from the name of its inventor "Hadfield" steel. It generally contains from

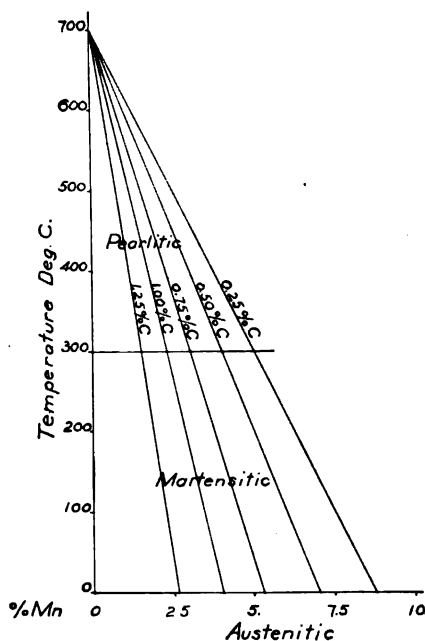


Fig. 321. — Influence of manganese and carbon on position of critical point A_{r1} and corresponding types of structure.

10 to 15 per cent manganese and from 1 to 1.5 per cent carbon. In its cast condition it is weak and has but little ductility probably because of the presence of a considerable quantity of free carbide. On being heated to a high temperature (1000 deg. C. or more), however, and quenched in water or oil its tenacity is greatly raised and it becomes very ductile; the treatment being often called on that account "water toughening." The marked change of properties resulting from it is probably due to the absorption of the carbide at a high temperature and its retention in solution by quick cooling. The structure of manganese steel both in its cast and in its water quenched condition is shown in Figures 322 to 325. In the cast sample the carbide is seen to occur as thick membranes surrounding the austenitic grains and here and there in chunks. The treated sample is nearly free from carbide and possesses the polyhedral structure characteristic of gamma iron and of austenite. The properties

of austenitic manganese steel are those of austenite, namely low elastic limit but great hardness and wearing power combined with much ductility.

Tungsten Steels. — Tungsten appears to raise rather than lower the critical points of iron while it forms with it a double carbide of iron and tungsten from which

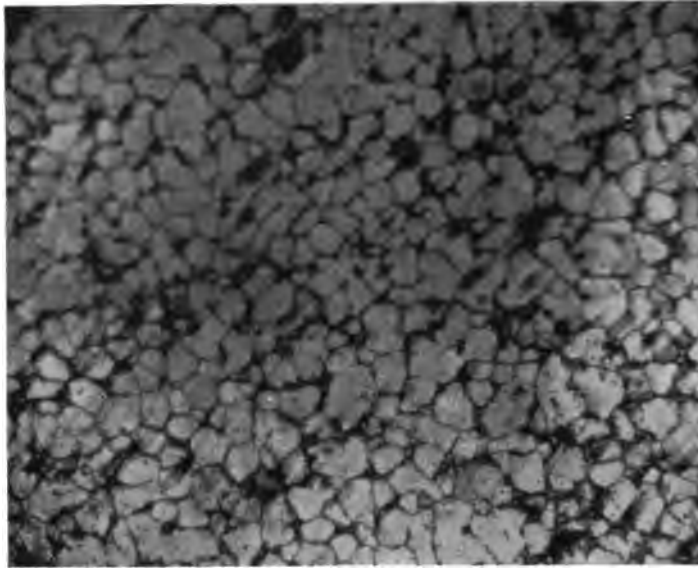


Fig. 322. — Manganese steel. Austenitic. Cast. Magnified 50 diameters.

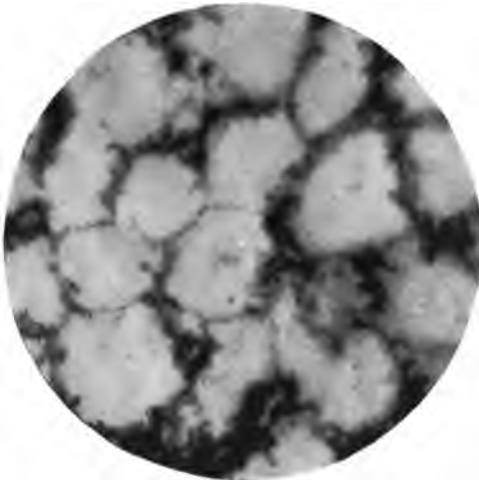


Fig. 323. — Same as in Figure 322. Magnified 300 diameters.



Fig. 324. — Manganese steel. Austenitic. Water quenched. Magnified 100 diameters.

it may be safely inferred that tungsten steels will at first remain pearlitic on slow cooling and that as the percentage of tungsten increases it will become cementitic, that is it will contain carbide particles. This is shown in Figure 326, which is a reproduction of the constitutional diagram of tungsten steels according to Guillet. In

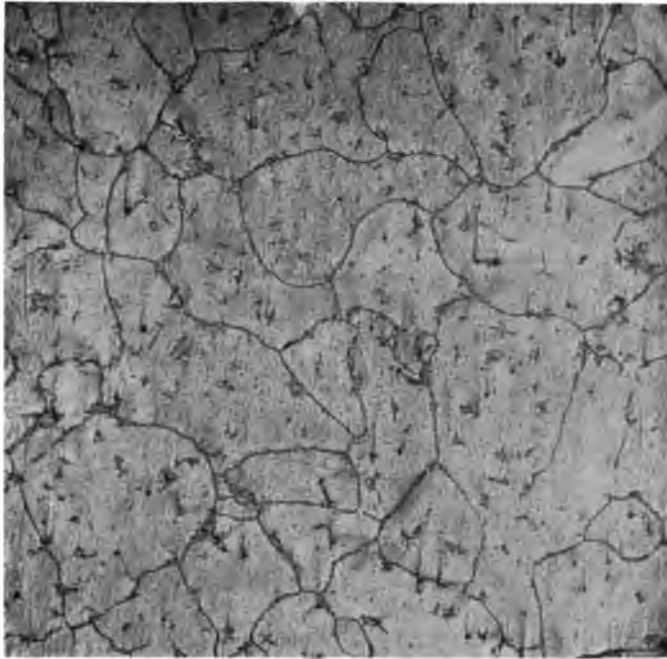


Fig. 325. — Manganese steel. Austenitic. Water quenched. Magnified 100 diameters.

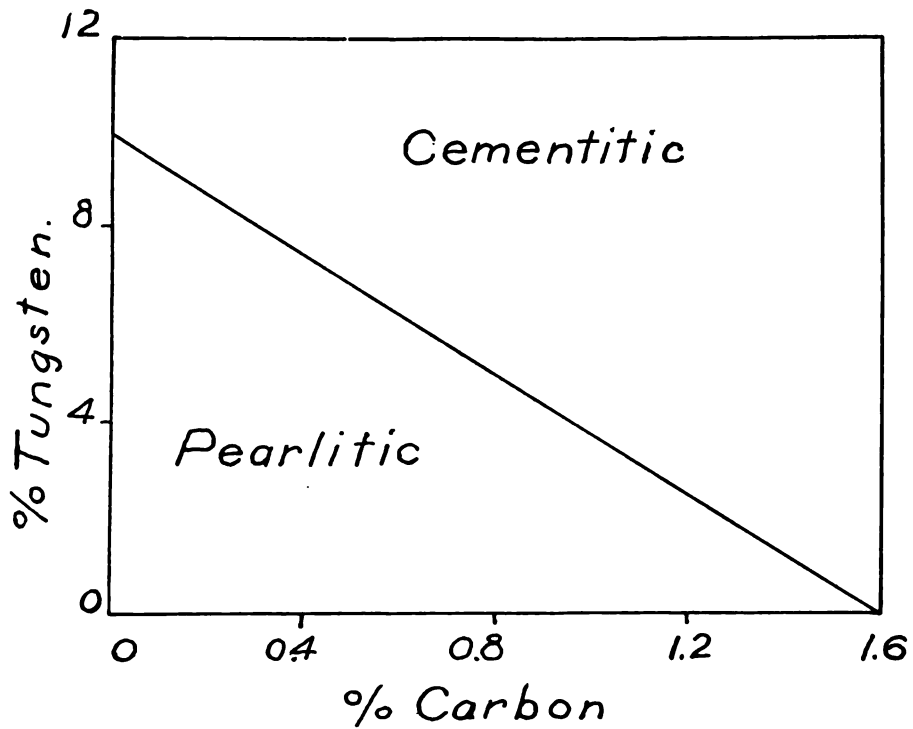


Fig. 326. — Tungsten steel. Constitutional diagram. (Guillet.)

the presence of a considerable proportion of tungsten, however, the position of the A_{r1} point seems to be greatly affected *by the temperature from which the steel cools*. Osmond, for instance, found in the case of a steel containing 0.42 per cent carbon and 6.25 per cent tungsten that heating to and cooling from some 900 deg. reveals the existence of two critical points respectively at 690 and 650 deg. As the temperature from which cooling begins increases, however, two interesting phenomena are observed, (1) the upper point occurs at practically the same temperature but becomes fainter and finally disappears and (2) the lower point remains pronounced but *its position is gradually lowered*. Cooling from 1015 deg., for instance, resulted in a faint critical point at 670 deg. while the lower point was depressed to 625 deg.; cooling from 1210 deg. caused the disappearance of the upper point while the lower remained very pronounced but now occurred at 500 degrees. Böhler, likewise experimenting with a steel containing 0.85 per cent carbon and 7.78 per cent tungsten, reports the exist-



Fig. 327. — Tungsten steel. Tungsten 27.75 per cent. Carbon 0.276 per cent. Magnified 200 diameters. (Guillet.)

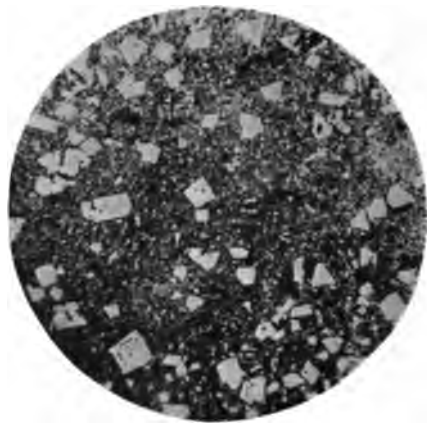


Fig. 328. — Tungsten steel. Tungsten 39.96 per cent. Carbon 0.867 per cent. Magnified 200 diameters. (Guillet.)

ence of a point at 710 deg. and one at 550 deg., the upper one, however, occurring only when the metal has not been heated above 1100 deg. while the second is only to be detected when the temperature exceeds 1000 deg. In other words on cooling from above 1100 deg. the lower point only occurs, on cooling from below 1000 deg. only the upper point is visible, while heating to and cooling from a temperature situated between 1000 and 1100 deg. causes the appearance of both points. It will be shown soon that this indirect influence of tungsten upon the critical points affords an explanation of the remarkable properties of self-hardening and high speed steels which are chiefly tungsten steels.

On heating cementitic tungsten steels to a high temperature the particles of free carbides are dissolved the more completely the higher the temperature. Air cooling is often sufficient to retain the carbides in solution while the metal becomes finely martensitic. Such steels are said to be "self-hardening."¹ The structure of two

¹ The presence of manganese or of a little chromium is necessary, however, to impart self-hardening properties to tungsten steel. The original "self-" or "air-hardening" steel, that is "Mushet" steel, always contained considerably more than 1 per cent manganese and was high in carbon.

cementitic tungsten steels is reproduced in Figures 327 and 328. The white particles are the double carbide.

Tungsten steels are used (1) for springs generally after hardening followed by tempering, (2) for magnets after hardening only, and (3) for tools as self-hardening steels. In the latter case, however, considerable manganese is always present, the resulting alloy being in reality a quaternary steel. High speed steels are quaternary steels generally containing a large proportion of tungsten; they will soon be described.

Chrome Steels. — Chromium forms double carbides with iron probably $x\text{Fe}_3\text{C}\cdot y\text{Cr}_3\text{C}_2$ or possibly solid solutions of the two carbides, while it has little if any direct influence on the position of the critical points.¹ The presence of chromium, however, like that of tungsten causes the point on cooling to be markedly lowered as the temperature from which the metal cools increases. Osmond, for instance, found the following relations between the maximum temperature and the position of the critical point on cooling:

MAXIMUM TEMPERATURE	CRITICAL POINT ON COOLING	MAXIMUM TEMPERATURE	CRITICAL POINT ON COOLING
835	713-716	1220	635-643
1030	682-692	1320	600-640

The constitutional diagram of chrome steels is shown in Figure 329 after Guillet. Reheating cementitic chrome steel to a high temperature followed by quick cooling (air or water) results generally in the disappearance of some of the particles of free carbide. The case hardening of chrome steels yields very hard cases. As the core coarsens, however, these steels should always receive the double treatment described in Chapter XIX, that is (1) reheating and quenching for refining the core and (2) reheating and quenching for refining and hardening the case.

The chrome steels that are utilized seldom contain more than 3 per cent chromium and are therefore pearlitic after slow cooling; they are used for the manufacture of armor-piercing projectiles, of steel balls, of files, and of some other tools, the presence of chromium increasing the hardness and the hardening power of the metal.

Becker writes that the hardness imparted by chromium is not accompanied by as much brittleness as that induced by carbon. According to the same author chromium also has the effect of increasing the elastic limit of steel, especially when it is combined with vanadium. The structure of pearlitic chromium steel resembles that of pearlitic carbon steel.

Vanadium Steels. — Vanadium forms double carbides² with iron and has no marked influence on the positions of the critical points. Unlike tungsten and chro-

¹ According to some recent observations of Nesselstrauss, chromium lowers the point A_1 of hypo-eutectoid steels, eventually causing its disappearance while it raises a little the point A_1 . The proportion of chromium needed to cause the point A_1 to disappear is the smaller, the higher the carbon content. With 0.20 per cent carbon, 5 per cent chromium are needed. With more carbon a correspondingly smaller percentage of chromium suffices. Recent experiments conducted at the Watertown Arsenal, Watertown, Mass., with steel containing 0.50 per cent carbon, also indicate that increasing the chromium content from 0 to 4.05 per cent raises the A_{c1} point from 743 to 791 deg. C. and the A_1 point from 671 to 748 deg. C.

² Arnold and Read believe that mixtures of carbide of iron (Fe_3C) and of carbide of vanadium (V_4C_4) are formed rather than double carbides. In alloys containing 6 per cent vanadium the carbide formed contains only vanadium according to these writers.

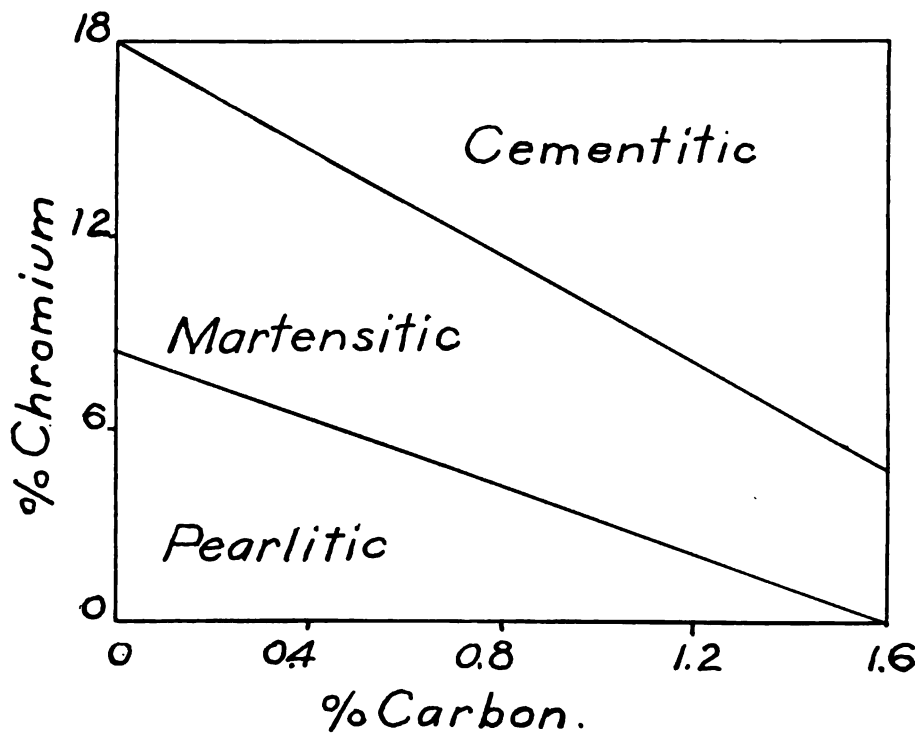


Fig. 329. — Chrome steel. Constitutional diagram. (Guillet.)

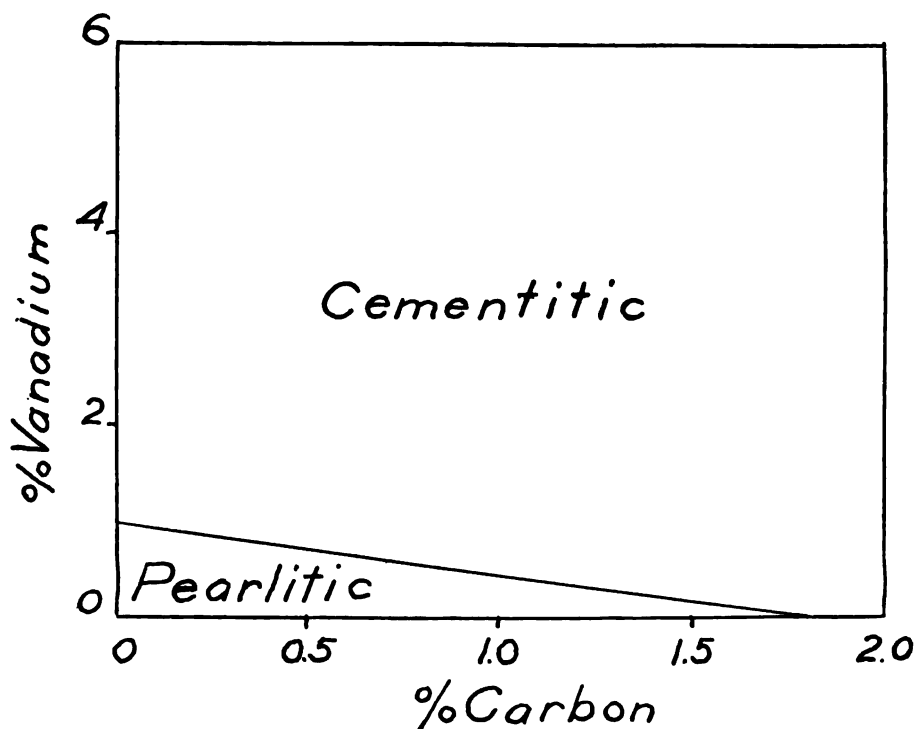


Fig. 330. — Vanadium steel. Constitutional diagram. (Guillet.)

mium it does not seem to cause the lowering of the A_r points with increasing temperature. The constitutional diagram of vanadium steels is shown in Figure 330 after Guillet. Two types of structures are produced, pearlitic and cementitic. Guillet describes the appearance of the particles of free carbide as being triangular.

According to Guillet heating cementitic vanadium steels to a high temperature fails to cause the absorption of the free carbide, vanadium steels differing in this respect from other steels in which double carbides are formed.

The vanadium steels commercially utilized seldom contain more than 1 per cent vanadium and are, therefore, pearlitic and free from carbides. Their proper-

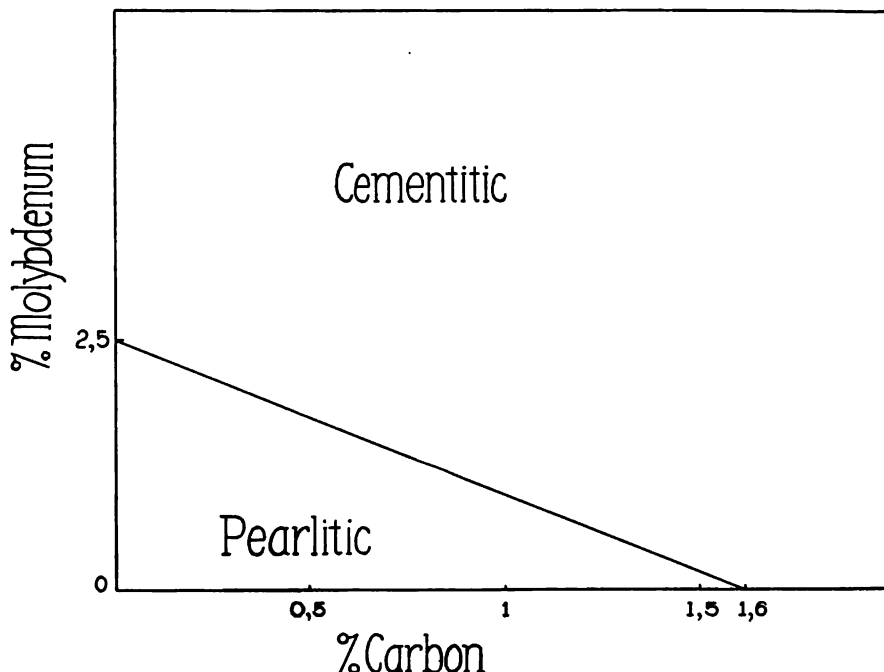


Fig. 331. — Molybdenum steel. Constitutional diagram. (Guillet.)

ties recall those of pearlitic nickel steels, namely high combination of elastic limit and ductility and greater resistance to shock, to alternate stresses, and to wear. The very small amount of vanadium sufficient to produce these results should be noted.

Molybdenum Steels. — The constitutional diagram of molybdenum steels is shown after Guillet in Figure 331. With increasing carbon and molybdenum, the steels which were at first pearlitic on slow cooling become cementitic. According to Thomas Swinden the A_{r1} point of these steels is steadily lowered as the temperature from which cooling starts increases, that lowering being the more marked the larger the percentages of molybdenum and carbon. The same author writes that molybdenum renders the pearlite very emulsified, even in annealed steel; that it lowers the saturation point, with 8 per cent molybdenum from 0.36 to 0.44 per cent carbon being sufficient for the exclusion of free ferrite; that any treatment involving slow cooling coarsens the structure and is very detrimental; that the chemical residue of

annealed molybdenum steel contains 91.7 per cent of the carbon present in the steel 89.5 per cent of the molybdenum, and generally more iron than is required by the formula Fe_3C , from which it is inferred that molybdenum is not combined with carbon but is present as an iron-molybdenum compound, and that there is no increase in hardness as molybdenum increases from 1 to 8 per cent.

According to Guillet molybdenum has an influence similar to that of tungsten on the physical properties and on the structure of steel but four times more intense.

Silicon Steels. — Silicon, probably as an iron silicide, FeSi , forms a solid solution with iron in all proportions and has no very marked influence upon the position of the

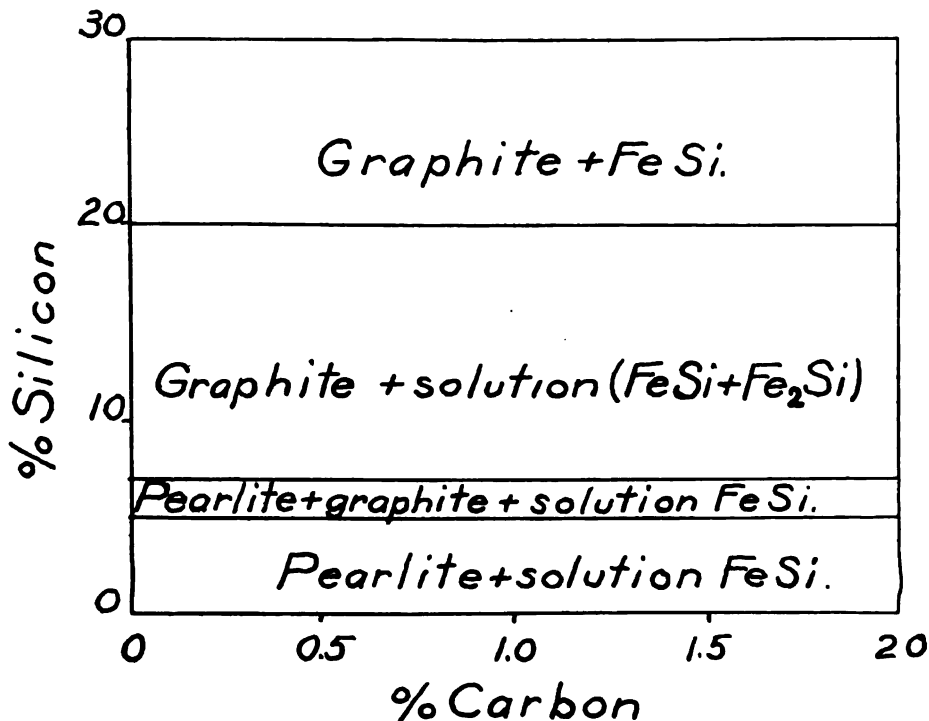


Fig. 332. — Silicon steel. Constitutional diagram. (Guillet.)

critical points from which we may infer that slowly cooled silicon steels will be neither martensitic nor cementitic. It is a well-known fact, moreover, that silicon has a marked tendency to cause the formation of graphitic carbon when present over a certain proportion especially in high carbon steel. The constitutional diagram of silicon steels is shown in Figure 332 according to Guillet. It will be seen that the structure is independent of the carbon content being entirely regulated by the proportion of silicon. As long as the proportion of silicon does not exceed 5 per cent the steel is pearlitic and the whole of the carbon remains in the combined condition. Between 5 and 7 per cent of silicon some pearlite is still present, and hence, some combined carbon, but graphitic carbon also occurs; between 7 and 20 per cent of silicon the whole of the carbon is in the graphitic condition, the balance of the steel consisting of a solid solution of the silicide FeSi in iron (silico-ferrite), and also, according to

Guillet, of some Fe_2Si likewise dissolved in iron. With more than 20 per cent of silicon the steel is composed of graphite and of FeSi .

It should be noted that the only silicon steels utilized contain less than 5 per cent of silicon and are, therefore, pearlitic and free from graphitic carbon unless indeed subjected to prolonged annealing or very slow cooling when some graphitic carbon will form, especially in high carbon steels. This formation of graphitic carbon takes place the more readily the higher the temperature, the longer the time at a high temperature, the more silicon and the more carbon in the steel.

Silicon steels are chiefly used in the construction of dynamos because of their low magnetic hysteresis and high permeability and, with the addition of quite a little manganese, for springs and for certain parts of automobiles.

Chrome-Nickel Steels. — From our knowledge of the constitution of nickel steels and of chromium steels it is possible to foretell the constitution of the quaternary chrome-nickel steels. Nickel steels being pearlitic-martensitic-austenitic and chrome steels being chiefly pearlitic-cementitic, we may expect that in chrome-nickel steels, as the proportions of carbon, nickel, and chromium increase the steels, at first pearlitic, will become in turn martensitic, austenitic, and cementitic. In the case of cementitic steels the free carbides will be embedded in a martensitic or austenitic matrix according to their composition. It should also be expected that increasing the proportion of nickel (and carbon) will cause the steel to pass from the pearlitic to the martensitic condition, etc., while increasing the chromium (and carbon) will make it cementitic. The presence of both nickel and chromium in the same steel produces a metal possessing the valuable qualities of both nickel and chromium steels, namely, high elastic limit combined with high ductility, greater hardness, hardening power, resilience, and better wearing qualities than carbon steels. Chrome-nickel steels are especially valuable in the construction of parts to be hardened and tempered when they yield a finely martensitic structure having greater shock-resisting power than the martensite of carbon steels. Practically the only chrome-nickel steels utilized are the pearlitic ones containing therefore moderate amounts of carbon, nickel, and chromium. They are used extensively in automobile construction and for the manufacture of armor plates. In the latter case, of course, one face of the plates is subjected to the case-hardening treatment. The case hardening of nickel-chromium steel resembles that of nickel steel. The metal should be reheated, after the case-hardening operation, slightly above the critical range of the case and quenched.¹ Because of the presence of nickel it is not so imperative to heat to and quench from a temperature superior to the critical range of the core before hardening the case, although such procedure would probably yield a tougher core.

Quaternary Vanadium Steels. — The introduction of a small amount of vanadium into the various special steels has been strongly urged and nickel-vanadium, chrome-vanadium, chrome-nickel-vanadium, and chrome-tungsten-vanadium steels have been used. It is claimed that the presence of a small proportion of vanadium (less than 0.50 per cent) increases the soundness of castings and their freedom from occluded gases and that it adds to the desirable physical qualities of forgings such as strength, resilience, ductility, etc. Guillet writes that nickel-vanadium steel properly hardened by quenching is relatively so tough that, unlike other hardened steels,

¹ Grenet states that the quenching of chrome-nickel steel may be done in boiling water saturated with salt, thus avoiding the possible distortions of more drastic treatment, while the metal is made very hard.

it does not require tempering. Since vanadium forms a double carbide with iron its presence in steel is likely to make it cementitic. In nickel steel and in nickel-chromium steel the matrix will be pearlitic, martensitic, or austenitic in accordance with the proportion of nickel and carbon present; in chrome steels it will be pearlitic or martensitic.

Chrome-Tungsten or High Speed Steels. — Slowly cooled chrome-tungsten steels are cementitic with a pearlitic, sorbitic, or even troostitic matrix. Upon being heated to a high temperature the carbide particles are dissolved, at least for the most part, and if the cooling that follows be sufficiently rapid they are retained in

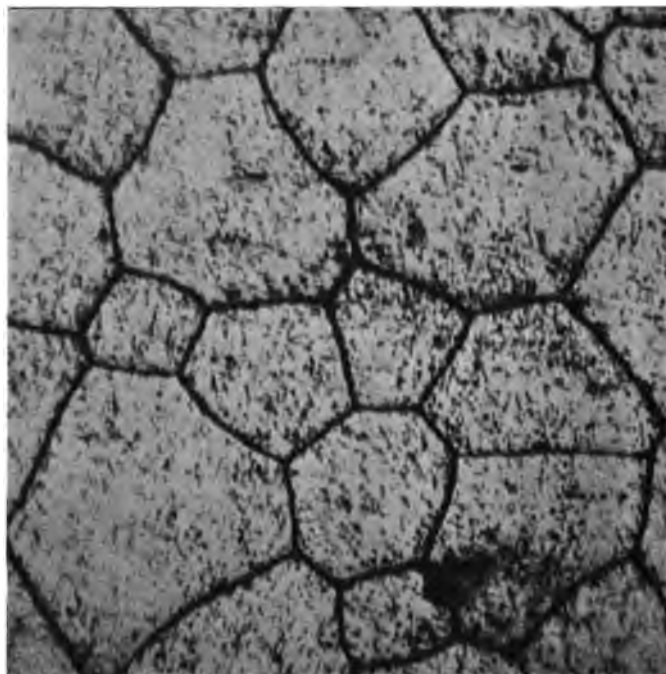


Fig. 333. — High speed steel. Quenched in air blast at 1160 deg. C. Magnified 500 diameters. Tungsten about 13 per cent. Chromium about 4 per cent. Carbon 0.46 per cent. (H. B. Pulsifer.)

solution, the metal acquiring a finely austenitic, martensitic, or austenite-martensitic structure. To cause a complete absorption of the free carbide, however, a very high temperature is often required, in some cases approaching the melting-point of the steel, while air cooling is frequently sufficiently rapid to prevent the carbide from again forming. After such treatment these steels although fully hardened are in a condition relatively so stable that they may be heated to a visibly red heat, i.e. to some 600 deg. C. before undergoing any marked transformation. This invaluable property makes it possible, with tools made of such steels suitably treated, to cut steel and other hard metals at such speed that the cutting edge of the tool becomes visibly red hot before breaking down. These steels are known in consequence as high speed steels. Their discovery by Taylor and White, at the time in

the employ of the Bethlehem Steel Company, South Bethlehem, Pennsylvania, marks one of the most distinct and revolutionary advances ever made in the metallurgy of iron and steel. The composition of these steels varies greatly: they may contain from 0.25 to 1 per cent carbon, generally not over 0.75 per cent; from 5 to 25 per cent of tungsten, generally between 10 and 20 per cent; from 2 to 10 per cent of chromium, generally between 2 and 8 per cent, and seldom over 0.40 per cent of manganese. Vanadium varying in amount between 0.25 and 1 per cent is now generally added.¹ In some types tungsten is replaced in part or wholly by molybdenum; in others a small amount of molybdenum is present in addition to the tungsten and chromium. Properly treated high speed steel often exhibits a polyhedral



Fig. 334. — High speed steel. Quenched at 1280 deg. C. Magnified 1500 diameters. Tungsten 17.87 per cent. Chromium 3.46 per cent. Vanadium 0.81 per cent. Carbon 0.65 per cent. (J. V. Emmons.)

(austenitic?) structure (Fig. 333) quite free from carbide particles. In the presence of large amounts of tungsten and chromium, however, some carbide remains undissolved even after rapid cooling from a temperature close to the melting-point of the metal (Fig. 334). The presence of a moderate amount of free carbide after the high heat treatment is not considered detrimental; on the contrary it appears to increase the cutting properties of the metal.

In the annealed condition the steel contains carbide particles which are probably the more numerous the larger the percentage of tungsten and chromium present (Figs. 335 and 336).

¹ According to Edwards 0.3 per cent vanadium allows a cutting speed 10 per cent greater, that is, permits the removal of 10 per cent more metal in the same time while with 0.20 per cent vanadium, 20 per cent more metal may be removed. The time between regrinding is also increased by vanadium.

The inventors of high speed steels recommended the following treatments as yielding the best results: (1) heating the tool slowly to about 815 deg. C., then quickly until its extreme edge showed indications of melting, (2) cooling the tool quickly to below 860 deg. and then quickly or slowly to atmospheric temperature, and (3) reheating the tool to about 640 deg. for five minutes (in a lead bath) followed by cooling in air. The author believes, however, that tools of high speed steel are now generally heated to near their melting-point followed by cooling freely in air, in an air blast, or in oil, a second treatment being rarely applied.

While the theories and hypotheses advanced to account for the remarkable properties of high speed steels differ greatly and while the true constitution of these

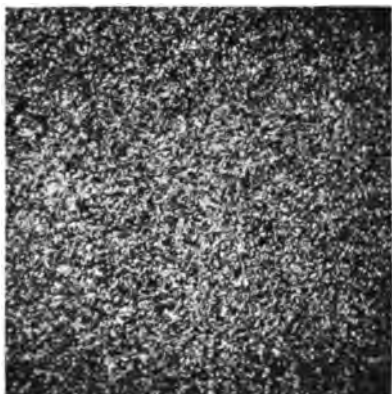


Fig. 335. — High speed steel. Typical structure after annealing. Magnified 150 diameters. (Edwards.)

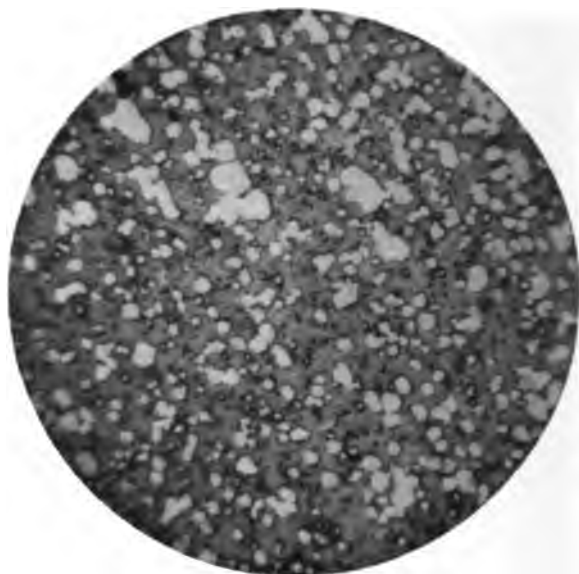


Fig. 336. — High speed steel. Annealed at 780 deg. C. Magnified 1500 diameters. Tungsten 18.36 per cent. Chromium 4.05 per cent. Vanadium 1.04 per cent. Carbon 0.59 per cent. (J. V. Emmons.)

steels is still to be discovered it seems certain that in order to produce what may be termed "high speed hardness" (1) a certain condition must be created by heating to a very high temperature and (2) that condition must be retained by quick cooling, since *both* high heating and quick cooling are essential to the production of high speed hardness. It has been argued that at a high temperature carbides are *formed* of great hardness and stability which upon being retained by quick cooling impart high speed properties to the steel, but it is now more generally held that the high temperature treatment results in the matrix of the steel *absorbing* all or nearly all the carbides, thereby acquiring great hardness which is retained if the carbides are prevented, through quick cooling, from again separating. This theory is better sustained by microscopical and other experimental evidences.

From the structure of treated high speed steel which is often polyhedral we naturally infer that the metal is in an austenitic condition. Other considerations, how-

ever, lead us also to believe that it is partly martensitic. We may consider its condition as martensite-austenitic. Purely austenitic steels like some manganese and nickel steels possess but little if any high speed hardness. To be sure it may be, as some have claimed, that in use the heat caused by the friction of the tool causes a tempering of the austenite into martensite, thereby increasing the hardness and hence the efficiency of the tool rather than softening it as would be the case with martensitic carbon steel. The fact that austenitic manganese and nickel steels behave differently might be explained on the ground that the austenite of which they are composed is less stable and therefore more readily converted first into martensite and then into sorbite with accompanying loss of hardness and hence of cutting power. Tungsten in other words, and chromium, appear to create a more stable condition, that is one resisting tempering much more effectively.

Clearly the fact that treated high speed steel is probably, to a large extent at least, austenitic, is not alone sufficient, in the light of our present knowledge, to account for its extraordinary cutting properties.

We naturally turn to the heating and cooling curves of high speed steel for additional information.

Mr. M. Yatsévitch of the Technical School of Kiev, Russia, has conducted in the author's laboratory an extensive investigation of the influence of heat treatment upon the position of the critical points of high speed steel. Over 100 heating and cooling curves were taken with a Saladin-Le Chatelier recording thermo-electric pyrometer. The most significant results are here briefly outlined. The steel used, kindly supplied by Dr. J. A. Mathews, had the following compositions: tungsten 18.20 per cent, chromium 3.00 per cent, vanadium 0.95 per cent, silicon 0.27 per cent, carbon 0.62 per cent, manganese 0.38 per cent, sulphur less than 0.025 per cent, and phosphorus less than 0.025 per cent. Heating curves obtained on heating this steel respectively to 920, 950, 1000, and 1050 deg. C. are shown in Figure 337 as well as the cooling curves resulting from slow, furnace cooling from these temperatures.

The heating curves exhibit two critical points respectively at about 775 and 855 deg. C. These points were found to be remarkably constant. Occurring as they do within such narrow range of temperature (some 80 deg. C.) it might be asked if instead of indicating two distinct transformations they do not correspond to two phases or stages of the same transformation.

The curves obtained on cooling slowly from 920 and 950 deg. C. respectively indicate a sharp evolution of heat occurring at 730 to 740 deg. C. and which we naturally infer to correspond to the opposite phase of the transformation or transformations occurring on heating as indicated by the heating curves. So long as the temperature reached on heating does not exceed 950 deg. C. the curves obtained on slow cooling are of the same type, i.e. they exhibit but one well-marked critical point at 730 to 740 deg. C. When, however, the maximum temperature on heating, which for brevity and following Howe, may be called T^{\max} reaches 1000 deg. C., this thermal point is slightly *lowered* while a second point occurs whose position although shifting somewhat, remains in the vicinity of 400 deg. C. (Fig. 337). As T^{\max} increases the upper point of the curve obtained on *slow* cooling decreases in intensity, while the intensity of the lower point increases. Bearing in mind that as T^{\max} increases we are approaching the treatment needed to confer high speed hardness we are justified in inferring that the transformations indicated by the upper point

on cooling must be thoroughly suppressed in order to obtain the desired results and that this suppression is to be brought about (1) by high heating and, as will be shown presently, (2) by rapid cooling.

The influence on the cooling curves of rapid cooling from increasingly high temperatures is clearly written in the curves shown in Figures 338 and 339. The curves

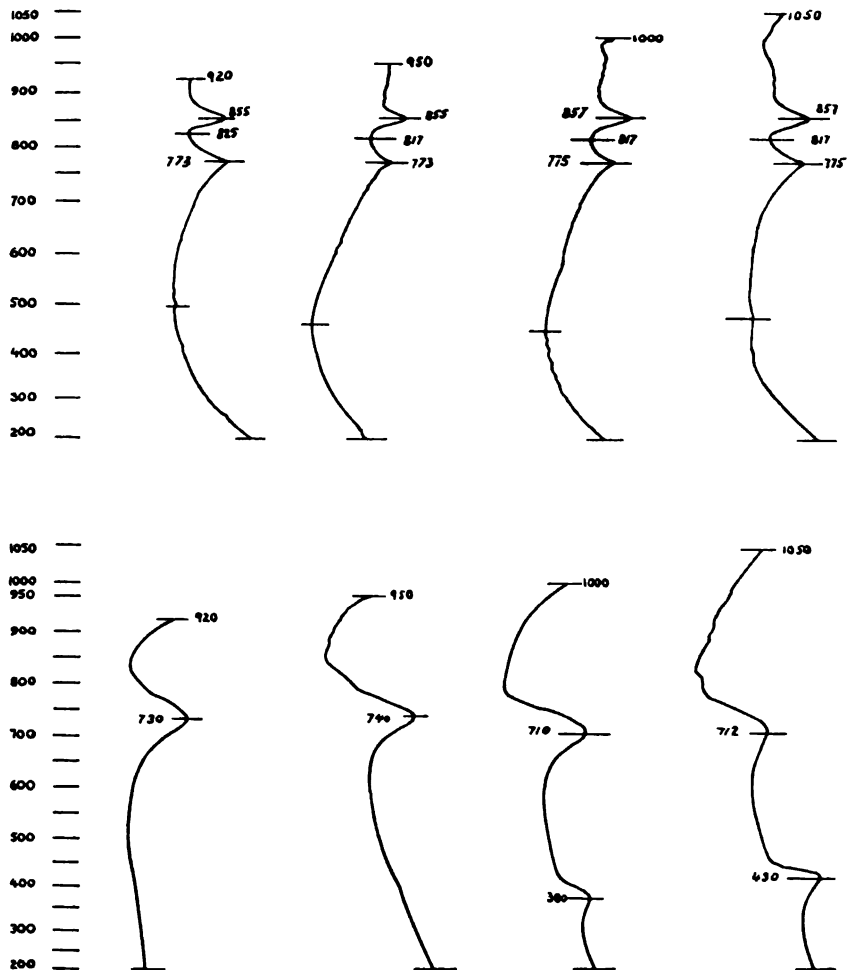


Fig. 337. — Heating and cooling curves of high speed steel. Slowly cooled in furnace. Time of cooling from 1000 to 200 deg. C., 132 minutes. (M. Yatsévitch in the author's laboratory.)

of Figure 338 were obtained by cooling freely in air the specimens and the tubes in which they were heated.

Those of Figure 339 by cooling in the same manner but more rapidly by means of a fan.

With the first rate of cooling (Fig. 338) it will be noted that (1) on cooling from 800 deg. C. but one sharply marked evolution of heat occurs on cooling at 665 deg.

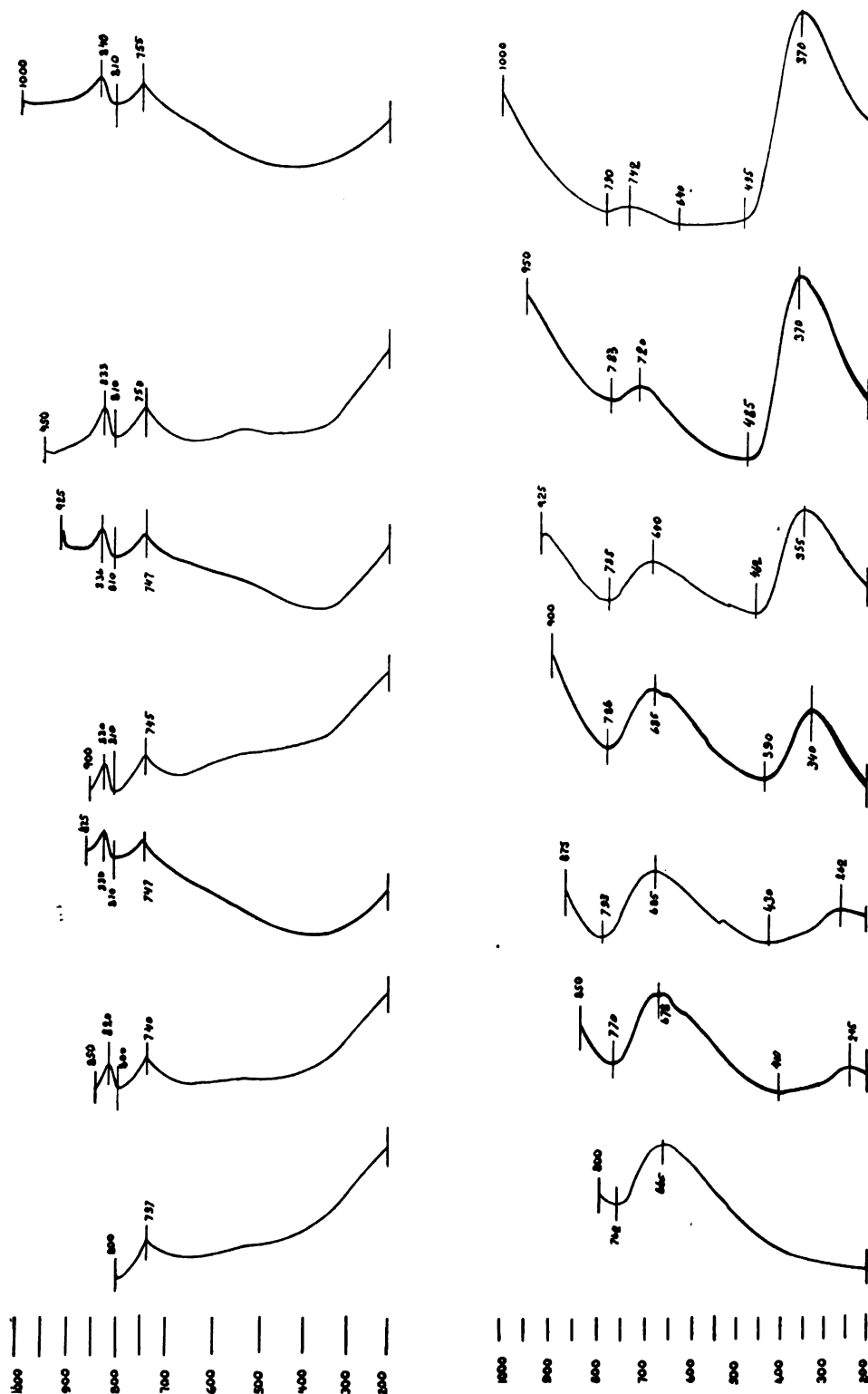


Fig. 338. — Heating and cooling curves of high speed steel. Samples cooled freely in air in the tubes holding them. Time of cooling from 1000 to 200 deg. C., 13½ minutes. (M. Yatskevitch in the author's laboratory.)

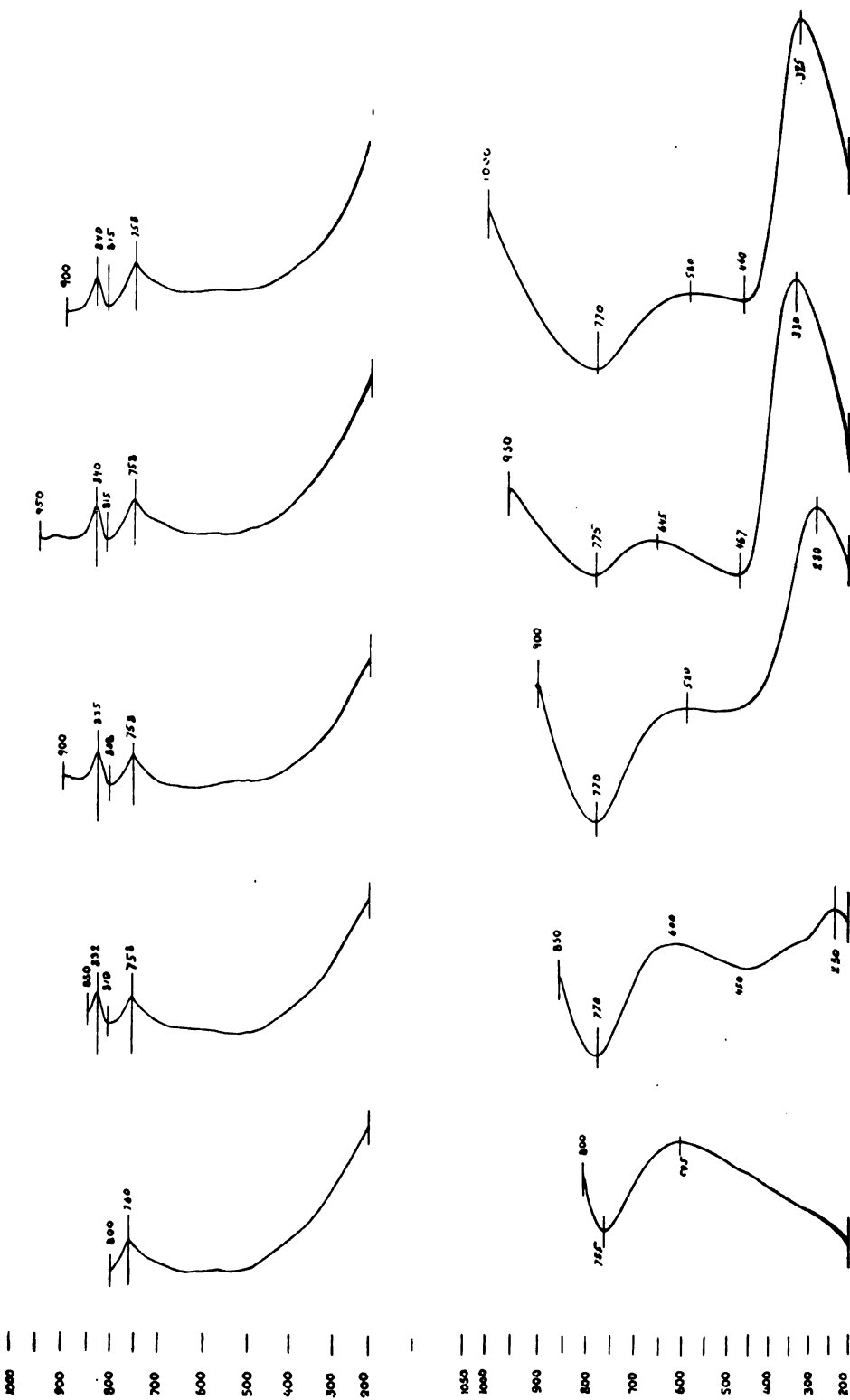


Fig. 339. — Heating and cooling curves of high speed steel. Samples cooled in air in the tubes holding them. Cooling hastened by fanning. Time of cooling from 1000 to 200 deg. C., 6¼ minutes. (M. Yatskevitch in the author's laboratory.)

C., (2) on cooling from 850, a critical point occurs in the curve at 245 deg. C., and (3) an increasing T^{\max} up to 1000 deg. C. the upper point on cooling is somewhat lifted but greatly decreases in intensity and shows signs of being finally eliminated, while the lower point is gradually raised to 370 deg. C. and becomes very intense. On cooling from 900 deg. C. the two points appear to have nearly the same intensity.

When cooling at the more rapid rate indicated by the curves of Figure 339 the same occurrences are observed but still more intensified. Cooling from 1000 deg. C. for instance shows an intense point at 395 deg. C. while the upper transformation if it still takes place is much more feeble besides being gradual and covering a wide range of temperature (730 to 460 deg. C.).

Summing up, it seems evident that with increasing T^{\max} and rate of cooling the upper critical point of the cooling curves is nearly, if not entirely, suppressed while the lower point grows enormously in intensity. The inference appears warranted that the treatment imparting high speed hardness suppresses, at least for the major part, a certain transformation occurring normally on slow cooling from moderately high temperatures at about 730 deg. C., while inducing with increasing magnitude a new transformation generally between 350 and 400 deg. C. The conclusion that the lower point is merely the upper point depressed by high heating and quick cooling would be untenable since the cooling curves show conclusively that the upper point is not lowered but merely decreases in intensity. As to the nature of the transformation apparently suppressed and of the transformation induced by the high speed treatment, any positive statement would be premature. We naturally connect the upper point with the separation of carbide on slow cooling but the cause of the lower point is still a matter for further investigation.

The etching of high speed steel was carefully investigated in the author's laboratory by Mr. M. Yatsevitch and the following conclusions appear warranted.

Alcoholic solution of picric and nitric acid may be used for etching high speed steel, at times with satisfactory results. Picric acid should be in the form of a saturated solution in alcohol and its action may be intensified by the addition of some 20 per cent of water. In the absence of water picric acid acts very slowly, the needed time of etching moreover increasing rapidly as the temperature from which the steel cools increases and as the speed of cooling increases, in other words as the conditions of the industrial treatment of high speed steel are approached. Picric acid etching is satisfactory for steel in the annealed condition as shown in Figure 340, where the bright particles of carbide are clearly revealed embedded in a dark matrix. The time of etching was 6 minutes. The same steel after high heat treatment could not be etched by picric acid even after a 48-hour immersion.

Nitric acid in alcohol (some 10 per cent acid) is less satisfactory for etching annealed specimens (Fig. 341) but much more effective in revealing the structure of heat-treated specimens (Fig. 342). Its action while much more rapid than that of picric acid also becomes decidedly slower as the temperature reached on heating and as the speed of cooling increases and therefore as the mineralogical hardness of the steel increases. The annealed specimen shown in Figure 341 was etched for 2 minutes while after high heat treatment (Fig. 342) an immersion of 14 minutes was required. It will be observed that both picric and nitric acid etching leave the free carbides bright while darkening the matrix and that nitric acid readily reveals the polyhedral structure of heat-treated samples. It is also apparent that the length of time needed to develop the structure of high speed steel is an indication of the heat

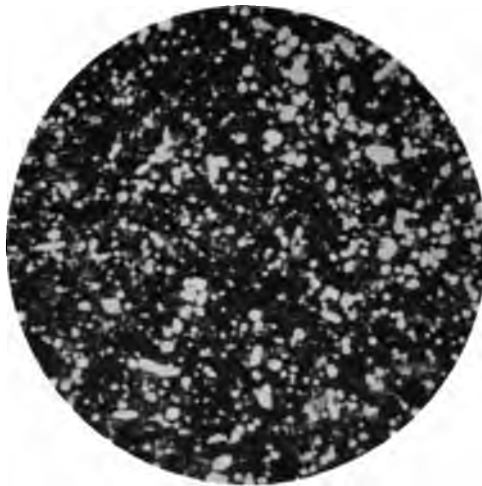


Fig. 340. — Annealed. Etched with picric acid six minutes.

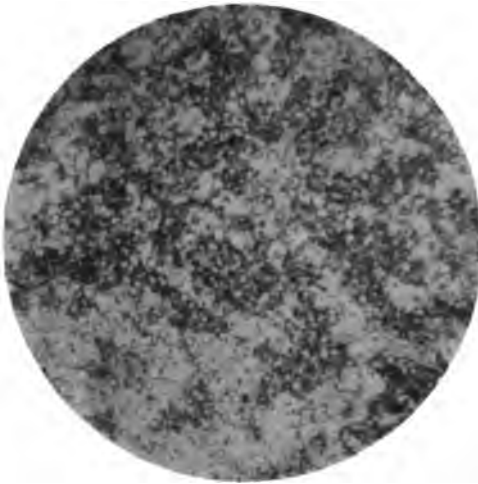


Fig. 341. — Annealed. Etched with nitric acid two minutes.

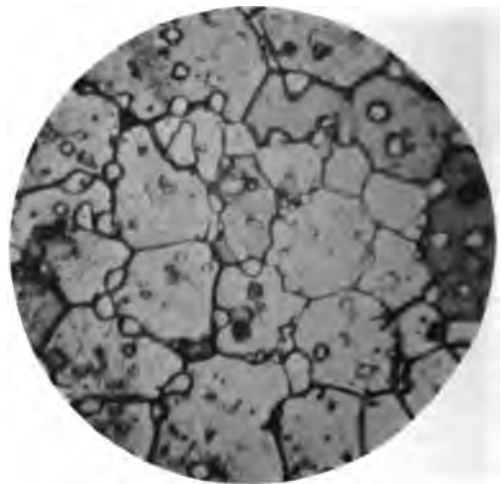


Fig. 342. — Heated to 1200 deg. C. and quickly cooled. Etched with nitric acid fourteen minutes.

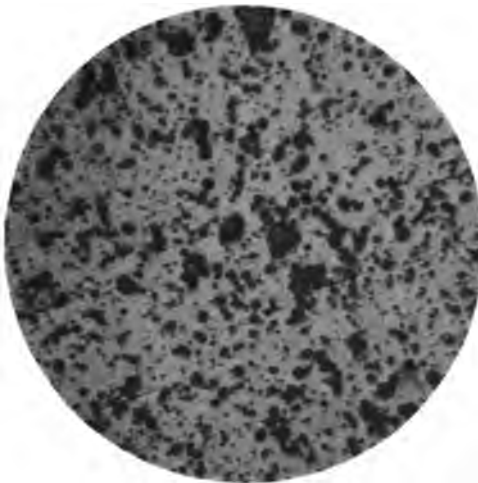


Fig. 343. — Annealed. Etched with hydrogen peroxide and sodium hydrate.

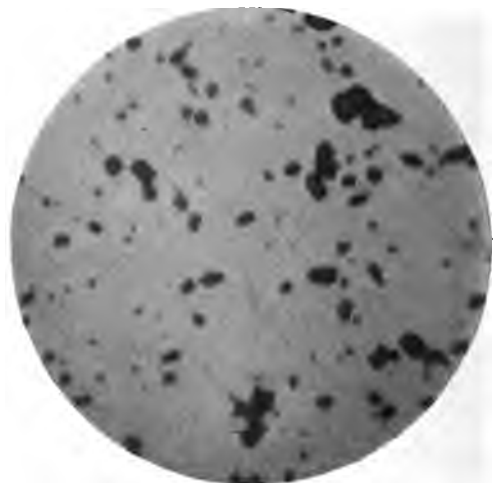


Fig. 344. — Heated to 1240 deg. C. and quickly cooled. Etched with hydrogen peroxide and sodium hydrate.

High speed steel. Tungsten 18.20 per cent, chromium 3 per cent, vanadium 0.95 per cent, carbon 0.62 per cent, silicon 0.27 per cent, manganese 0.38 per cent. All photomicrographs are magnified 980 diameters. (M. Yatsevitch in the author's laboratory.)

treatment it has received. Obviously, increasing temperature and speed of cooling produce in the matrix of high speed steel changes which are not brought out in the etched structure of the metal but which are made apparent by a much greater resistance to the action of picric and nitric acid and also by increased mineralogical hardness.

As briefly described in Chapter II, Mr. Yatsevitch has obtained interesting and valuable results in using for etching high speed steel a solution of hydrogen peroxide and sodium hydrate. This reagent etches the particles of free carbide *dark* while leaving the matrix white and brilliant even after prolonged immersion (Figs. 343



Fig. 345. — Magnified 86 diameters.



Fig. 346. — Magnified 980 diameters.

High speed steel. Cast. Etched with hydrogen peroxide and sodium hydrate.
(M. Yatsevitch in the author's laboratory.)

and 344). The etching time (about 10 to 15 minutes) remains the same regardless of the heat treatment applied. The method affords a sure means of revealing the existence of the free carbide to the exclusion of everything else. It does not reveal the polyhedral structure of the steel after high heat treatment, clearly because the net surrounding the grains does not indicate the presence around them of membranes of free carbide.

The cast structure of the high speed steel used in these experiments is illustrated in Figures 345 and 346. It may be safely inferred that the constituent colored dark by the Yatsevitch reagent is the carbide and that the latter forms a component therefore of the eutectic or eutectoid evidently present in the cast metal.

CHAPTER XXII

CAST IRON

Cast iron differs from steel in being deprived of malleability. This lack of malleability is due to the presence of a large quantity of carbon, generally between 2.50 and 4.00 per cent. The carbon present in cast iron may be (1) wholly in the graphitic condition, (2) wholly in the combined condition, and (3) partly in the graphitic and partly in the combined condition. These three types of cast iron should be separately considered. The solubility of carbon in iron and the factors influencing the formation of graphite or of combined carbon should, however, first be considered.

Solubility of Carbon in Iron. — Slightly above its melting-point (1500 deg. C.) pure iron does not appear to be able to dissolve more than some 5 per cent carbon. As its temperature increases, however, its saturation point for carbon increases materially. O. Ruff and O. Goecke report the following results:

TEMPERATURE DEG. C.	PER CENT CARBON DISSOLVED
1135	4.30
1220	4.50
1305	4.81
1522	5.46
1623	5.78
1823	6.59
2020	6.95
2122	7.51
2169	8.21
2220	9.60
2271	8.97
2320	8.61
2420	8.09
2475	7.78
2626	7.45

Hanemann has reported the following saturation points.

TEMPERATURE DEG. C.	PER CENT CARBON DISSOLVED
1133	4.25
1350	4.50
1620	5.40
1880	6.18

Iron saturated with carbon is reported to boil at 2750 deg. while pure iron boils at a much lower temperature.

Ruff's and Goecke's results are shown graphically in Figure 347. Hanemann's

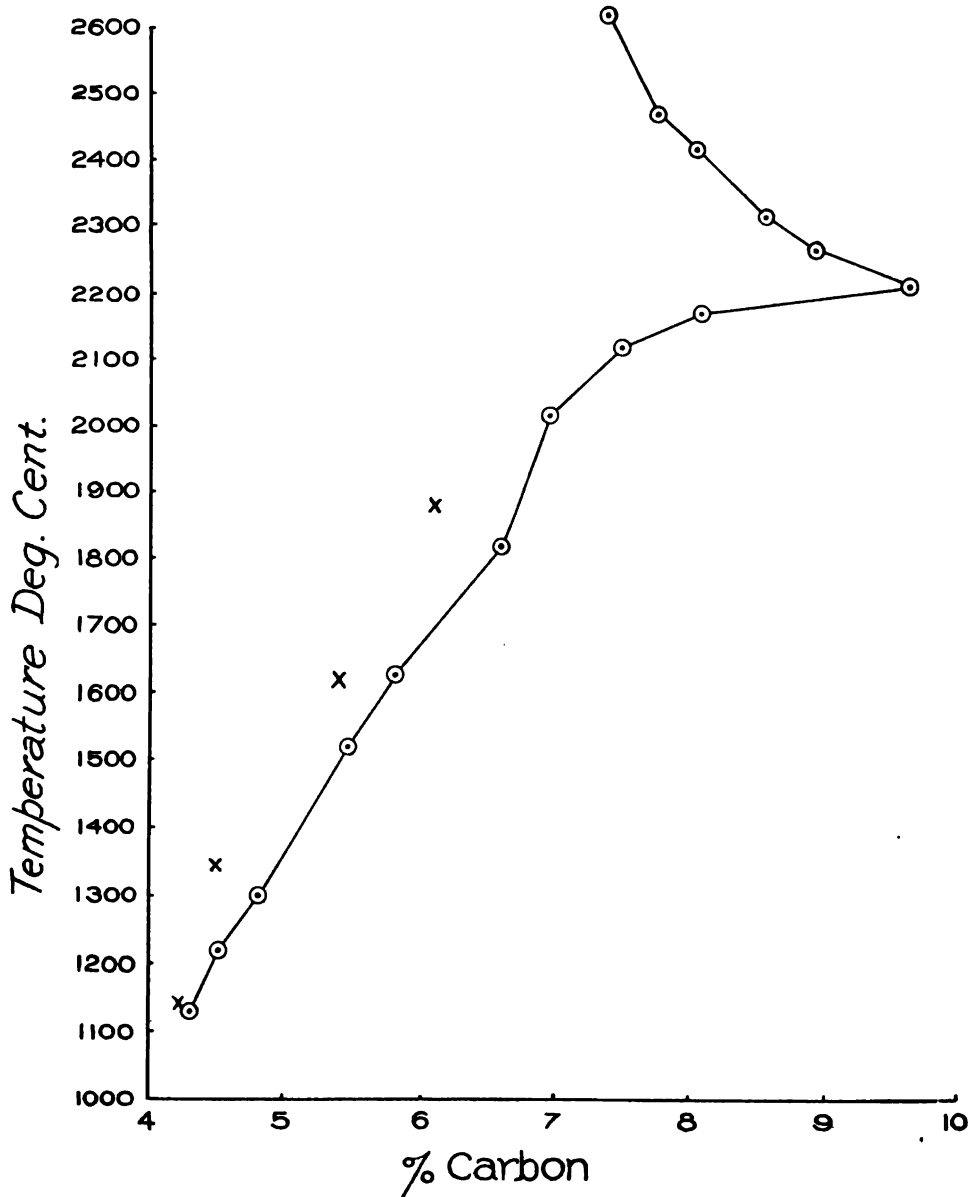
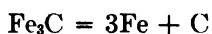


Fig. 347. — Solubility of carbon in iron.

results are indicated by crosses in the same diagram. Since the carbide Fe_3C , or cementite contains 6.67 per cent carbon, it may be inferred from the results tabulated above, (1) that iron-carbon alloys saturated with carbon consist between 1130

(the melting-point of the eutectic as later explained) and 1823 deg. of liquid solutions of iron and Fe_3C , the proportion of the latter constituent increasing with the temperature, and (2) that at 1823 the alloy is liquid Fe_3C . From the fact that the amount of carbon dissolved at 2220 deg. C., namely 9.60 per cent, is the amount called for by the carbide Fe_2C it is further inferred (1) that between 1823 and 2220 deg. the alloys are liquid solutions of Fe_3C and Fe_2C the latter increasing and the former decreasing with the temperature, and (2) that at 2220 deg. the alloy is liquid Fe_2C . At higher temperature some of the Fe_2C breaks up into iron and graphite ($\text{Fe}_2\text{C} = 2\text{Fe} + \text{C}$) the resulting graphite floating to the top of the liquid bath, thus explaining the smaller and decreasing proportions of dissolved carbon at temperatures exceeding 2220 deg. The break in the curve at 1823 (Fig. 347) corresponds to the formation of Fe_3C , the break at 2220 deg. to the formation of Fe_2C . Taking iron with its maximum proportion of carbon namely at 2220 deg. when it is capable of dissolving 9.60 per cent carbon, as previously stated, it then consists of liquid Fe_2C . On cooling it is not capable of retaining so much carbon some of it being rejected as graphite through the transformation of some of the Fe_2C into Fe_3C and graphite ($3\text{Fe}_2\text{C} = 2\text{Fe}_3\text{C} + \text{C}$). This formation of Fe_3C at the expense of Fe_2C with rejection of graphite continues until at 1823 deg. Fe_3C only is present (6.69 per cent carbon). On further cooling the alloy must continue to reject carbon, now through the transformation of some of the Fe_3C into iron and graphite ($\text{Fe}_3\text{C} = 3\text{Fe} + \text{C}$) a transformation which continues until a temperature of 1130 deg. is reached when the alloy contains 4.30 per cent carbon and when further cooling now causes its solidification. The possibility of the carbide Fe_3C solidifying out of the liquid solution being later converted wholly or in part into iron and graphite will be considered in the following pages.

Formation of Combined and Graphitic Carbon. — It will be explained in Chapter XXVI that when cast iron solidifies the carbon probably remains in the combined condition and that the resulting carbide, Fe_3C , is partly free and partly in solid solution in the iron. This Fe_3C , however, is an unstable compound and when formed at a high temperature it is readily decomposed into graphite and iron according to the reaction



hence the formation of graphitic carbon in cast iron. Two factors are conspicuous in promoting the formation of graphitic carbon, (1) a slow rate of cooling through and below the solidification period and (2) the presence of silicon. The gray, i.e. graphitic, cast irons are generally those which have been cast in sand and hence slowly cooled and which contain a relatively large percentage of silicon. It follows that under otherwise identical conditions and compositions a large casting will become more graphitic on solidifying than a smaller one since it will cool more slowly; also that of two castings of equal size, cooled under like conditions and of identical composition except as to their silicon contents, the one richer in silicon will contain more graphitic carbon. The conditions most effective in preventing the formation of graphitic carbon and in promoting, therefore, the retention of carbon in its combined form are (1) quick rate of cooling through and below the solidification range and (2) the presence of much sulphur or manganese.

Cast Iron Containing only Graphitic Carbon. — Cast irons containing a considerable amount of graphitic carbon are known as gray cast irons because of the appear-

ance of their fracture which is grayish or blackish and coarsely crystalline. Cast irons containing the whole of their carbon in the graphitic condition and therefore free from combined carbon are extreme types seldom produced. Their structure, however, should be considered.

Proceeding as we did in the case of steel we shall first assume cast iron to be a pure alloy of iron and carbon, free, therefore, from its usual impurities. If the whole of the carbon is in the graphitic condition it is evident that cast iron can only contain the two constituents graphite and iron or ferrite. We may therefore anticipate its structure. It will, however, be interesting to study the mode of occurrence of the



Fig. 348. — Gray cast iron free from combined carbon. Magnified 100 diameters. Not etched. (F. C. Langenberg in the author's laboratory.)

graphitic carbon. The structure of cast iron practically free from combined carbon is illustrated both before and after etching in Figures 348 and 349. The metal will be seen to consist of an iron or ferrite matrix in which are embedded many irregular and generally elongated and curved plates of graphite. These graphite plates break up so effectively the continuity of the metallic mass as to completely destroy the ductility and malleability of a substance (ferrite) by nature very ductile and malleable. The brittleness of high graphitic cast iron is not due so much to the brittleness of the graphite it contains nor even to its large proportion of graphite as to the thorough manner in which the continuity of its otherwise ductile matrix is destroyed by the shape and distribution of the graphite particles.

It will be seen in another chapter that when the graphite occurs in small rounded particles as it does in malleable cast iron the ferrite matrix may retain considerable ductility and malleability.

The ferrite matrix of this highly graphitic cast iron (Fig. 349) will be seen to be made up of the polyhedral crystalline grains characteristic of carbonless iron, the ferrite of cast iron being similar in this and other respects to the ferrite of wrought iron and of hypo-eutectoid steel. In impure cast iron it undoubtedly holds in solution silicon and possibly, to some extent, other impurities.

Highly graphitic cast iron is brittle and deprived of ductility and malleability because of the presence of numerous plates of graphitic carbon; it is weak because of the presence of graphite plates and because of the relative weakness of its matrix; it is soft and therefore easily machined because of the softness both of its matrix and of the graphite it contains; it expands on solidifying because of the formation, with



Fig. 349. — Same metal as in Figure 348. Magnified 100 diameters. Etched. (F. C. Langenberg in the author's laboratory.)

increase of bulk, during solidification of a large amount of graphitic carbon. It should be noted that because of its low specific gravity graphite will occupy a relatively large proportion of the bulk of the metal. Cast iron, for instance, containing by weight 3 per cent of graphite contains by volume some 12 per cent of that element.

As might be expected the rate of solidification and further cooling has some influence both upon the shape and size of the graphite particles as well as upon the size of the ferrite grains, and therefore upon the physical properties of the metal, very slow solidification promoting the formation of large graphite plates and of large ferrite grains. Were it possible to cause the graphite in cast iron to occur in small rounded particles instead of sharp, curved plates, its ductility and strength would undoubtedly be greatly increased.

The diagram of Figure 350 shows graphically the structural composition of iron-

carbon alloys in which the whole of the carbon occurs as graphite. Only those alloys, however, containing from 3 to 4.5 per cent carbon can be produced. Indeed in the absence of silicon even these are quite unobtainable. With less than 3 per cent carbon it is well nigh impossible to prevent the retention of some combined carbon, while with less than 2 or at least with less than 1.50 per cent carbon the whole of the carbon is likely to be in the combined condition. The diagram, therefore, is only a theoretical one. It has, nevertheless, its interest for it will be shown in another chap-

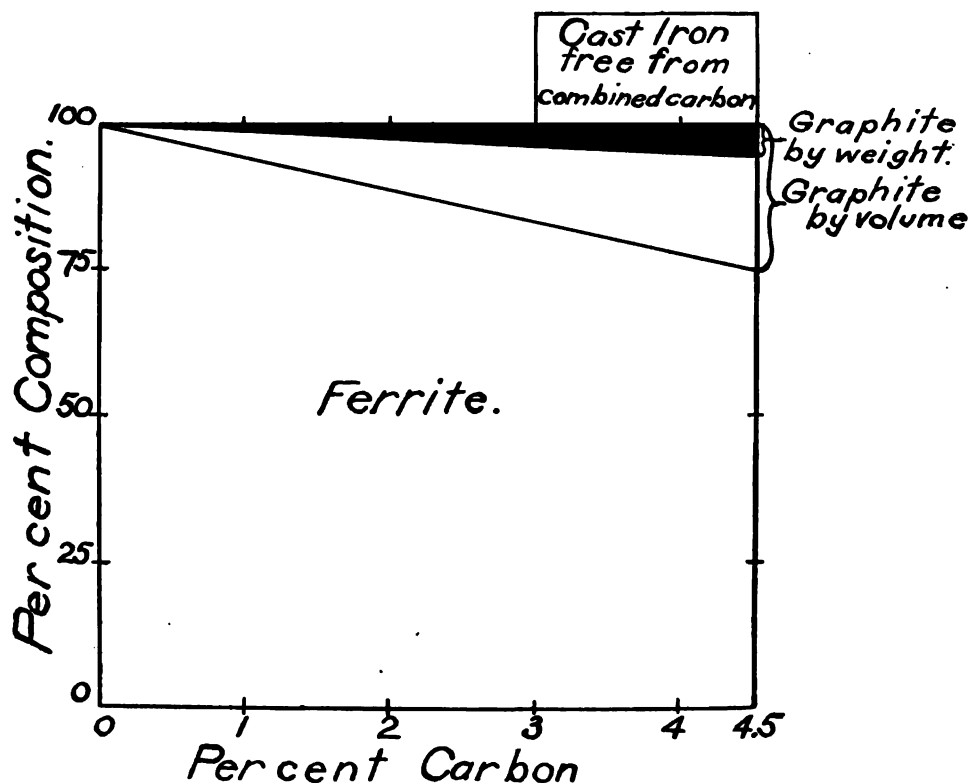


Fig. 350. — Structural composition diagram of iron-carbon alloys free from combined carbon.

ter to represent the stable and final equilibrium of the iron-carbon system. The percentage of graphite by volume has also been indicated.

Cast Iron Containing only Combined Carbon. — Cast iron containing only combined carbon and free, therefore, from graphitic carbon is called “white” cast iron from the aspect of its fracture which is white, brilliant, and highly metallic. The absence of graphitic carbon is generally due (1) to the presence of much manganese and sulphur and of little silicon, (2) to quick cooling through and below the solidification period, or (3) to both low silicon, high manganese and sulphur, and quick solidification. Cast iron, for instance, may contain so much sulphur and manganese and so little silicon as to be white even after slow solidification or it may solidify so quickly as to be white even in the presence of much silicon and little manganese and sulphur.

A familiar instance of the marked influence of the rate of cooling is afforded by

the casting in the metal molds of casting machines of cast iron which if cast in sand would have been gray, whereas it is now white. Small castings since they cool more quickly become white more readily than larger ones.

In the absence of graphitic carbon the structure of cast iron should resemble the structure of a very high carbon steel, i.e. it should consist after slow cooling of pearlite and of a large amount of free cementite. This is found to be the case as shown in Figure 351 in which is illustrated the structure of white iron containing about 3 per cent of combined carbon. Theoretically this alloy should contain nearly 63 per cent of pearlite and 37 per cent of free cementite. The dark constituent in the photograph is pearlite, the light one, visibly in relief, cementite. The structure of white cast iron is also shown in Figure 352 under high magnification, the laminations of pearlite being clearly seen. The structure of white cast iron is further illustrated in Figures



Fig. 351. — White cast iron. Magnified 56 diameters.



Fig. 352. — White cast iron. Magnified 500 diameters. (Wüst.)

353 and 354 after Guillet. These photomicrographs are reproduced here because they afford an interesting example of the action of sodium picrate (Chapter VIII) in coloring free cementite while leaving pearlite uncolored.

The structural composition of white cast iron is to be calculated like the composition of any hyper-eutectoid steel of known carbon content as explained in Chapter VIII, the following relation existing between the percentage of pearlite and that of carbon in the iron, on the assumption that pearlite contains 0.834 per cent carbon:

$$P = \frac{800 - 120 C}{7}$$

the balance of the metal being of course free cementite. While structurally it resembles high carbon steel, white cast iron is deprived of malleability being indeed very brittle and very hard. This brittleness and hardness are due to the very large proportion of free cementite present which itself is very hard and brittle.

It will be evident that, starting from carbonless iron, as the carbon increases at first low carbon steel is produced and then in succession medium high carbon steel, high carbon steel, and finally white cast iron, each metal passing gradually into the next without any sharp line of demarcation between them. It is logical to base the distinction between high carbon steel and white cast iron upon the malleability of the former and the non-malleability of the latter and this is altogether a question of carbon content. The dividing line may be drawn somewhat arbitrarily at 2 per cent carbon. As a matter of fact steels are very seldom manufactured containing more than 1.75 per cent carbon while white cast iron rarely contains less than 2.25 per cent carbon. Between the steel series, therefore, and the white cast-iron series there is a natural gap, the existence of which generally removes any doubt as to the nature of the metal under examination.

Again if the process of manufacture be known there need be no doubt as to the classification of any highly carburized iron alloy: if made in the blast furnace from



Fig. 353. — White cast iron. Magnified 200 diameters. Etched with picric acid. (Guillet.)

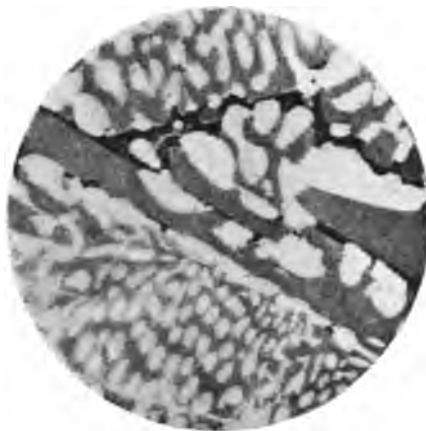


Fig. 354. — Same metal as in Fig. 353. Magnified 200 diameters. Etched with sodium picrate. (Guillet.)

the reduction of iron ore, it is cast iron, while if it is the product of refining cast iron (by the Bessemer or the open hearth processes), or of the remelting under oxidizing conditions of iron or steel scrap with or without cast iron (open hearth process), or of the carburizing of wrought iron (cementation process), or of the carburizing and melting of wrought iron (crucible process), it is steel.

The diagram of Figure 355 indicates graphically the structural composition both proximate and ultimate of any iron-carbon alloy containing from 0 to 6.67 per cent *combined* carbon, that is, from 100 per cent ferrite to 100 per cent cementite assuming as it has been done before that pearlite contains 0.834 per cent carbon.

It will be noted that two sources of ferrite are indicated in the diagram, namely, (1) pearlite (eutectoid) ferrite and (2) pro-eutectoid or free ferrite, the sum of both being known as total ferrite, while four sources of cementite are to be considered, namely, (1) pearlite (eutectoid) cementite, (2) pro-eutectoid cementite, (3) eutectic cementite, and (4) pro-eutectic cementite, the sum of all four being known as total

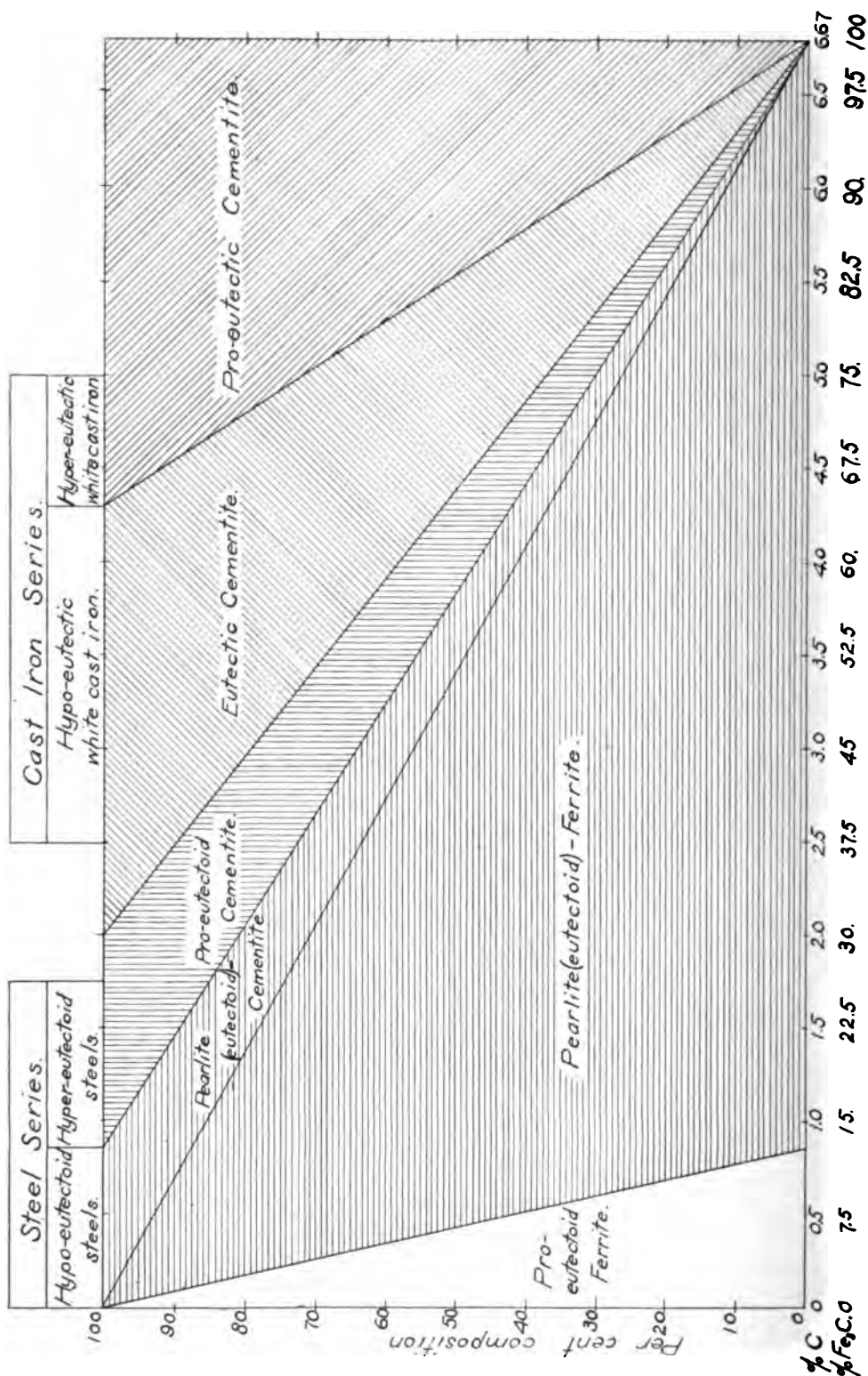


Fig. 355. — Structural composition diagram of iron-carbon alloys free from graphitic carbon.

cementite and that of (2), (3), and (4) as free cementite. Let us recall the meaning of these terms:

Pearlite or eutectoid ferrite is the ferrite included in pearlite.

Free or pro-eutectoid ferrite is the ferrite liberated as hypo-eutectoid steel cools slowly from its upper critical point (A_{r3} or $A_{r3.2}$) to its lower point (A_{r1}).

Pearlite or eutectoid cementite is the cementite included in pearlite.

Pro-eutectoid cementite is the cementite that is liberated as hyper-eutectoid metal cools slowly from its upper critical point ($A_{r_{em}}$) to its lower point ($A_{r3.2.1}$).

Eutectic cementite is the cementite included in the austenite-cementite eutectic which forms at the end of the solidification of alloys containing more than some 1.70 per cent carbon as explained in Chapter XXVI.

Pro-eutectic cementite is the cementite which forms between the beginning and the end of the solidification of alloys containing more than 4.3 per cent carbon as explained in Chapter XXVI. Howe calls it "primary" cementite.¹

The portions of the diagram corresponding respectively to the steel series and to the white cast-iron series have also been indicated leaving two groups of alloys unrepresented by industrial products, namely, those containing between 1.70 per cent and 2.25 per cent carbon and those containing more than 5 per cent of carbon.² The steel portion of this diagram has been used in Chapter VIII.

Cast Iron Containing both Combined and Graphitic Carbon. — Cast-iron castings nearly always contain both combined and graphitic carbon. In the majority of cases they contain from 0.25 to 1.50 per cent of combined carbon, the balance of that element being in the graphitic condition. The chief factors affecting this distribution of carbon between the combined and the graphitic states have already been alluded to; they are (1) the rate of cooling during and below solidification (hence the size of the castings) and (2) the presence of silicon, manganese, and sulphur, the first element promoting, and the last two opposing, the formation of graphitic carbon. If it be considered (1) that graphitic carbon is soft, (2) that the presence of much graphite, since it implies little combined carbon, means the occurrence of soft ferrite in the cast iron, (3) that combined carbon (cementite) is very hard, and (4) as later explained, that the presence of combined carbon, at least up to a certain proportion, greatly increases the strength of cast iron, it will be evident that the physical properties of cast iron, especially its strength and hardness, will depend chiefly upon the proportion of combined and graphitic carbon it contains.

Let us first consider the structure of cast iron containing a small amount, say 0.25 per cent, of combined carbon and some 3 per cent of graphitic carbon (Fig. 356). The combined carbon will yield 15 times its own weight of cementite ($0.25 \times 15 = 3.75$

¹ Howe questions the actual existence of commercial hyper-eutectic white cast iron on the ground that pro-eutectic cementite, as later explained, is so rapidly converted into graphite that it cannot be retained unless indeed by extremely quick cooling or in the presence of much manganese.

² It should be remembered that we are considering here pure alloys of iron and carbon. In the presence of much manganese (or chromium) iron may contain as much as 6.50 per cent and even much more carbon, while in their absence cast iron very seldom contains more than 4.5 per cent carbon. Again some unimportant products are offered for sale under the name of semi-steel which may contain between 1.75 and 2.50 per cent of total carbon entirely combined, forming, therefore, a sort of connecting link between the steel and the cast-iron series. They are frequently obtained by remelting cast iron in cupola furnaces in the presence of considerable iron or steel scrap. Washed metal likewise may contain between 1.75 and 2.50 per cent of total and entirely combined carbon but this is a semi-finished product resulting from a partial refining only of cast iron.

per cent) and the resulting pearlite 8 times its own weight of cementite ($3.75 \times 8 = 30$ per cent), or more quickly,

$$0.25 \times 120 = 30 \text{ per cent pearlite}$$

exactly as in the case of steel.

The cast iron under consideration will therefore contain 30 per cent pearlite, 3 per cent of graphite, and the balance, 67 per cent, necessarily free ferrite. Cast iron containing graphitic carbon may be considered as being made up of two distinct parts, namely, (1) graphite and (2) a metallic matrix in which the graphite particles are embedded. It will be obvious, moreover, that the metallic matrix of gray cast iron is in reality a steel matrix since it necessarily consists, like steel, of an aggregate



Fig. 356. — Gray cast iron. Hypo-eutectoid matrix (0.25 per cent combined carbon). Magnified 100 diameters. (Boylston.)

of ferrite and cementite partly associated to form pearlite. In cast iron free from combined carbon the matrix is pure ferrite; with a little combined carbon it is of the nature of a low carbon steel; as the combined carbon increases the metallic matrix is converted into steel of increasing carbon content; with less than some 0.80 per cent carbon the matrix resembles an hypo-eutectoid steel; with some 0.80 per cent carbon the matrix is pure pearlite, i.e. eutectoid steel; with more than 0.80 per cent carbon some free cementite is formed, the matrix consisting of hyper-eutectoid steel. In other words, as the proportion of combined carbon increases, structural changes take place in the metallic matrix of cast iron identical to those observed and described in the case of steel. The structure of cast iron containing increasing proportion of combined carbon is illustrated in Figures 356 to 358.

The above considerations justify us in considering gray cast iron as steel, that is, as an aggregate of ferrite and cementite, the continuity of which is destroyed by the presence of numerous graphite plates, the enormous difference in properties between cast iron and steel being due solely to the presence of this graphitic carbon or rather

to the breaking of the continuity of the mass which it implies. To illustrate further, if it were possible to remove bodily from a chunk of cast iron every particle of graphite, its strength and ductility would not probably be greatly increased because its continuity would still be effectively destroyed by the empty spaces once occupied by graphite. If not too high in carbon, however, it would now be weldable and could be forged into a small piece of steel, or it could be remelted and cast into a sound steel casting.

Mottled Cast Iron. — Cast irons are sometimes produced that are partly gray and partly white, that is, made up of particles containing graphitic carbon and of particles



Fig. 357. — Gray cast iron. Eutectoid matrix. Magnified 500 diameters. (Boylston.)



Fig. 358. — Gray cast iron. Hyper-eutectoid matrix. Magnified 500 diameters. (Wüst.)

free from graphite. Their structure is well shown in Figure 359. They are called "mottled" because of the appearance of their fracture.

Structural Composition of Cast Iron. — The structural composition of any cast iron of known percentages of graphitic and combined carbon and considered as a pure alloy of iron and carbon can readily be calculated by following the method employed in the case of steel and assuming pearlite to contain 0.834 per cent carbon, that is, exactly 1 part by weight of cementite and 7 parts of ferrite. It should be noted, however, that in the presence of graphite it requires a smaller proportion of carbon to convert the whole matrix into pearlite since there is less iron to be so converted. To make the matter clear in order that cast iron may be free from both excess ferrite and excess cementite it must contain ferrite and cementite in the exact proportion of 1 part of cementite to 7 of ferrite. If the cast iron contains G per cent of graphite and C per cent of combined carbon forming $15C$ per cent of cementite the balance of the metal, $100 - G - 15C$, will be ferrite. Consequently if

$$100 - G - 15C = 7 \times 15C = 105C$$

$$\text{or } 100 - G - 120C = 0$$

that is, if the proportion of ferrite equals 7 times that of cementite the matrix will contain pearlite only; if $100 - G - 120C$ is greater than 0 the matrix will be hypo-eutectoid; if $100 - G - 120C$ is smaller than 0 the matrix will be hyper-eutectoid. In the presence of 3 per cent graphite, for instance, the following relation will indicate the needed percentage of combined carbon to make the matrix entirely pearlitic:

$$100 - 3 - 120C = 0$$

which gives for C very nearly 0.80 per cent.

It will be sufficiently accurate to assume in every case that gray cast iron containing less than 0.80 per cent combined carbon has an hypo-eutectoid matrix while cast iron containing more combined carbon has an hyper-eutectoid matrix.

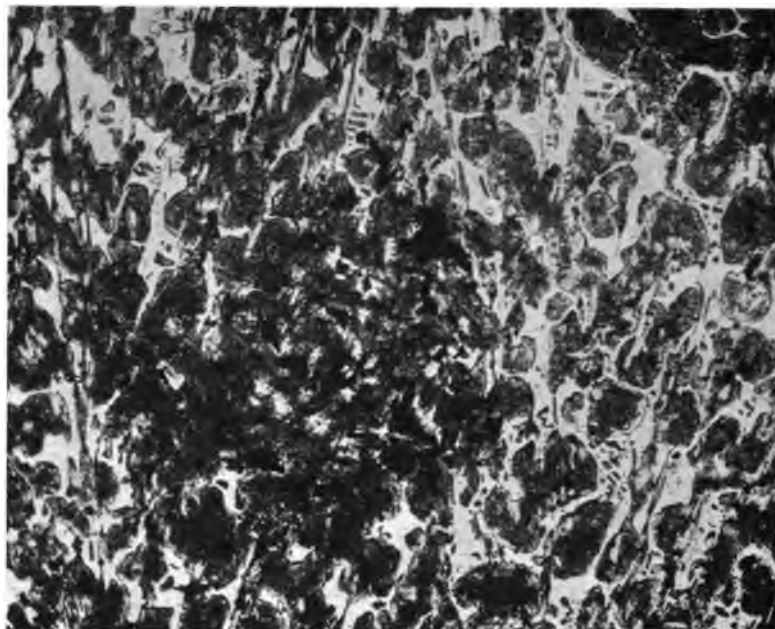


Fig. 359. — Mottled iron. Magnified 100 diameters. (Boylston.)

In calculating the structural composition of cast iron two cases then should be considered, (1) the cast iron contains less than 0.80 per cent combined carbon; it has an hypo-eutectoid matrix and (2) it contains more than 0.80 per cent combined carbon; it has an hyper-eutectoid matrix. In the first instance we have the following relations between the percentage of graphitic carbon, G, the percentage of combined carbon, C, the percentage of ferrite, F, and the percentage of pearlite, P,

$$(1) F + P + G = 100$$

$$(2) P = 8 \times 15C = 120C$$

If C = 0.50 per cent, for instance, and G = 3 per cent, the iron would contain 60 per cent pearlite, 37 per cent ferrite, and 3 per cent graphite.

If the iron has an hyper-eutectoid matrix, that is, if it contains more than 0.80

per cent of combined carbon, we can write the following equations, C_m representing the percentage of free cementite,

$$(1) P + C_m + G = 100$$

$$(2) P = \frac{8}{7}F = \frac{8}{7}(100 - G - 15C)$$

the second equation expressing the fact that the totality of the ferrite ($100 - G - 15C$) is included in the pearlite and that the percentage of pearlite is equal to $\frac{8}{7}$ times that of ferrite. If cast iron contains 2 per cent of graphite and 1.25 per cent of combined carbon, for instance, the foregoing equations indicate the following structural composition: pearlite 90.60 per cent, free cementite 7.40 per cent, and graphite 2 per cent.

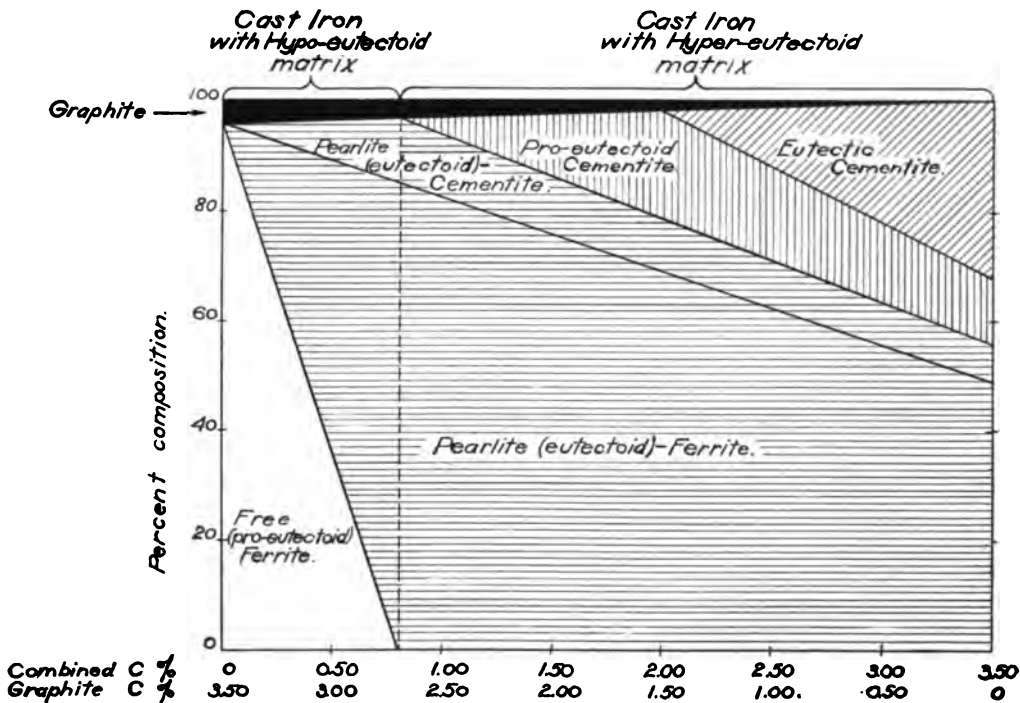


Fig. 360. — Structural composition diagram of iron-carbon alloys containing a constant proportion of total carbon (3.50 per cent), but varying percentages of combined carbon (from 0 to 3.50 per cent).

The structural, graphical diagram of cast iron containing both combined and graphitic carbon has been constructed in Figure 360 in accordance with the scheme followed in these chapters. It is assumed in this diagram that the total carbon remains constant at 3.50 per cent and that the amount of combined carbon increases from 0 to 3.50 per cent, in this way including the two extreme cases corresponding respectively to absence of combined carbon and of graphitic carbon. If this diagram be compared with that of the structural composition of steel, Chapter VIII, the steel nature of the metallic matrix of cast iron will be apparent. It will be noted that in the present diagram when the proportion of combined carbon exceeds 1.7 per cent there are two sources of free cementite indicated, namely, pro-eutectoid cementite

and eutectic cementite; the origin of the latter will be made clear in Chapter XXVI. Both of these cementites constitute the free cementite present in cast iron, containing more than 1.7 per cent of combined carbon; while formed, as later explained, at different periods of the cooling, they appear to coagulate together and cannot be distinguished from each other under the microscope.

Physical Properties of Cast Iron vs. its Structural Composition. — The physical properties of cast iron must necessarily depend to a very great extent upon the properties of its steel matrix from which it follows that its hardness and strength will increase with increasing combined carbon, the hardness indefinitely, the strength up to the eutectoid carbon ratio. It is evident, therefore, that cast iron of maximum strength (1) should have a steel matrix of maximum strength, i.e. should contain in the vicinity of 0.80 per cent combined carbon and (2) should contain as little graphitic carbon as possible since every graphite particle is a source of weakness; in other words, the nearer cast iron approaches a steel of maximum strength the greater will be its strength. After having secured the desired amount of combined carbon to give strength it is evident that a reduction of the graphitic carbon must mean a corresponding reduction of the total carbon in cast iron. In ordinary cupola practise for the production of cast-iron castings, however, which consists in remelting pig iron of suitable composition, the proportion of total carbon is difficult to control, being necessarily between 3 and 4 per cent and we must depend to produce strength almost altogether upon the retention in the combined condition of a suitable proportion of carbon. The total carbon may be decreased, however, by the use of iron and steel scrap as part of the burden of the cupola resulting in increased strength, for same percentage of combined carbon, or by remelting in a so-called "air furnace," i.e. under oxidizing conditions when part of the carbon is burnt out. These low total carbon, and therefore tenacious, cast-iron castings are sometimes offered for sale under the name of semi-steels, a practise somewhat misleading for they are not steel in any sense of the word since they are not malleable, have very little ductility, and generally contain a considerable amount of graphitic carbon.

If soft cast-iron castings are desired so that they may be easily machined they should contain as little combined carbon as possible. In the presence of but little combined carbon, however, the iron will not be very tenacious, strength and softness being antagonistic. If the castings are to be hard they should contain much combined carbon and, therefore, little graphite. In extreme cases they will be free from graphite, when their hardness will be very great, but they will then also be very brittle. In the majority of cases castings are wanted soft enough to be easily machined and at the same time of fair strength. This combination of properties is evidently to be obtained by producing a matrix corresponding to a medium high carbon steel, i.e. by causing the cast iron to retain some 0.30 to 0.60 per cent of combined carbon.

The percentage of combined carbon in cast iron upon which its physical properties primarily depend, can be ascertained more quickly and readily by microscopical examination than by chemical analysis and quite as accurately.

Chilled Cast-Iron Castings. — It is sometimes desired to produce cast-iron castings very hard near their outside but soft and relatively tough near their center. This may be done by so regulating the composition and solidification as to prevent the formation of graphite in those portions that should be hard while allowing it to form in the portions that should be soft. The means generally employed consist in using iron plates for those parts of the molds corresponding to the parts of the castings that

are to be hard and sand for the other parts, the quicker solidification and further cooling of the metal coming in contact with the iron plates causing the retention of much combined carbon. The resulting castings are known as "chilled" castings. Important instances of the application of this method are to be found in the manufacture of chilled cast-iron wheels and of chilled rolls. It will be evident that the presence of sulphur and manganese in the cast iron should promote the retention of combined carbon on quick cooling while the presence of silicon and of large percentages of total carbon should hinder it. The chemical composition of cast iron to be converted into chilled castings should therefore be carefully regulated. Microscopical examination should prove of much value in examining the depth and quality of "chills."

Cast Iron of Eutectic Composition. — The alloy of iron and carbon containing 4.30 per cent carbon has the lowest melting-point (1130 deg. C.) of all alloys of that

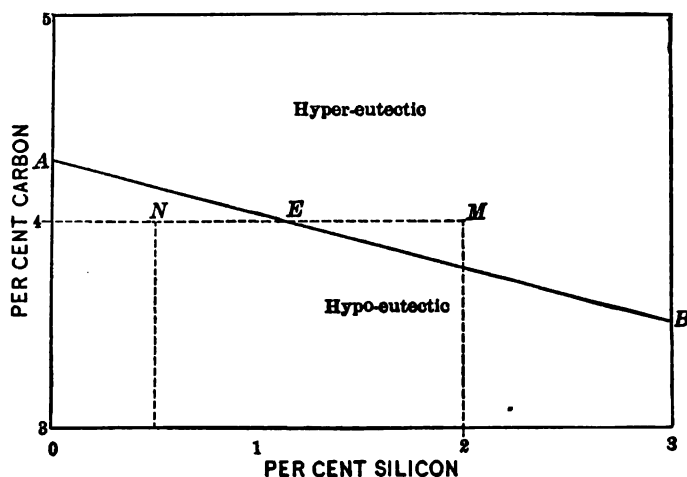


Fig. 361. — Influence of silicon-content on the percentage of carbon in the eutectic alloy.

series and is consequently known as eutectic alloy. The nature of eutectic alloys will be made clear in Chapter XXV. Those alloys solidify at a constant temperature whereas the solidification of alloys containing more or less carbon than the eutectic ratio covers a range of temperature which increases in width as the composition of the alloy is farther removed from that of the eutectic as explained in Chapter XXVI. In other words eutectic alloys pass quickly from the liquid to the solid state while hypo- and hyper-eutectic alloys pass through a pasty or semi-fluid period which may be of considerable duration, a condition, as later explained, which must be favorable to the formation of large graphite particles.

Eutectic Cast Iron vs. Impurities. — While as stated in the preceding paragraph the eutectic point for pure alloys of iron and carbon corresponds to 4.30 per cent carbon it is quite certain that some at least of the impurities always present in commercial cast iron affect in a marked degree the percentage of carbon needed to produce the eutectic alloy, i.e. the alloy of lowest melting-point, generally reducing the needed amount of carbon. From the work of Wüst and Petersen, for instance, we are led to infer that the presence of 1 per cent of silicon lowers that carbon some 0.30 per cent.

These authors' results may profitably be represented graphically as shown in Figure 361. The meaning of the diagram is obvious. The line *AB* divides cast iron into hyper- and hypo-eutectic metal according to its percentages of carbon and silicon. With 4 per cent of carbon and 2 per cent of silicon, for instance, the cast iron is hyper-eutectic, since its composition is represented by the point *M* in the hyper-eutectic range, while with the same amount of carbon but in the presence of only 0.5 per cent of silicon, the metal is hypo-eutectic, since its composition is represented by the point *N* in the hypo-eutectic range; with 3 per cent silicon some 3.50 per cent carbon suffices to produce the eutectic alloy, etc.

The Strength of Cast Iron vs. the Size and Form of the Graphite Particles. — Attention has already been called to the fact that the strength of cast iron is not only affected by the amount of carbon present but also, and in a marked degree, by the size and form of the graphite particles, long, curved plates of that constituent, for instance, being much more effective in reducing the strength than small rounded particles.

Eutectic Cast Iron vs. the Size and Form of the Graphite Particles. — It seems probable, as more fully explained in Chapter XXVI, that the bulk of the graphite present in cast iron forms during its solidification and since eutectic cast iron solidifies quickly while its temperature remains constant whereas the solidification of hypo- and hyper-eutectic alloys cover wider ranges of falling temperature it seems reasonable to infer as already pointed out that in eutectic cast iron the graphite must occur in smaller and more rounded particles. In other words the mushy, semi-fluid condition of relatively long duration assumed by non-eutectic alloys on solidifying must promote the formation of coarse graphite particles. If this view is correct it follows that for otherwise like composition and like treatment, cast iron of eutectic composition should be the strongest. In following that line of thought the influence exerted by some impurities on the eutectic carbon ratio should not be overlooked. With some 2 to 3 per cent silicon, for instance, some 3.50 to 3.75 per cent carbon should yield the eutectic alloy.

Silicon and Rate of Cooling vs. the Matrix of Cast Iron and the Formation of Graphite. — It is well known that the presence of silicon in cast iron promotes the formation of graphitic carbon while a rapid rate of cooling during solidification opposes it and causes it to occur in particles of smaller size.

The combined action of the rate of cooling and of the silicon content in determining the character of the matrix of cast iron may be advantageously shown graphically as in Figure 362. The abscissæ correspond to percentages of silicon, the ordinates to rates of cooling represented by arbitrary numbers, 2 indicating quicker cooling than 1, 3 quicker cooling than 2, etc. Any point on the line *AB* corresponds to a set of conditions producing a eutectoid matrix, while any point above *AB* refers to rates of cooling and silicon contents resulting in hyper-eutectoid, and below *AB*, in hypo-eutectoid matrix. The point *M*, for instance, on *AB* corresponds to 1 per cent of Si and a rate of cooling represented by 1.5, while *N* corresponds to 3 per cent of Si and a quicker rate of cooling, 4.4. Both sets of conditions will produce castings having a eutectoid matrix *but not identical properties, because the quicker cooling in the latter case must produce smaller and less angular graphite particles and hence a stronger metal.*

Cast Iron of Maximum Strength. — From the foregoing considerations the following conclusions may be drawn: (1) to possess maximum strength, cast iron should be

of eutectic composition because the graphite particles will then be smaller which in turn makes for greater strength, (2) the eutectic structure should be produced by high silicon and low carbon content since the latter promotes strength, (3) the cast iron should have a eutectoid matrix because it is the matrix of greatest strength, and (4) the eutectoid matrix should be produced by high silicon content and rapid cooling because the latter leads to the formation of small graphite particles.

Solidification of Eutectic Cast Iron. — The mechanism of the solidification of eutectic cast iron and of its subsequent transformation on slow cooling may be illustrated graphically as shown in Figure 363, assuming that no graphite forms. *ABCD* represents a block of eutectic cast iron cooling from above its melting-point to atmospheric temperature. Above its liquidus-solidus line *EF* the metal is liquid. On

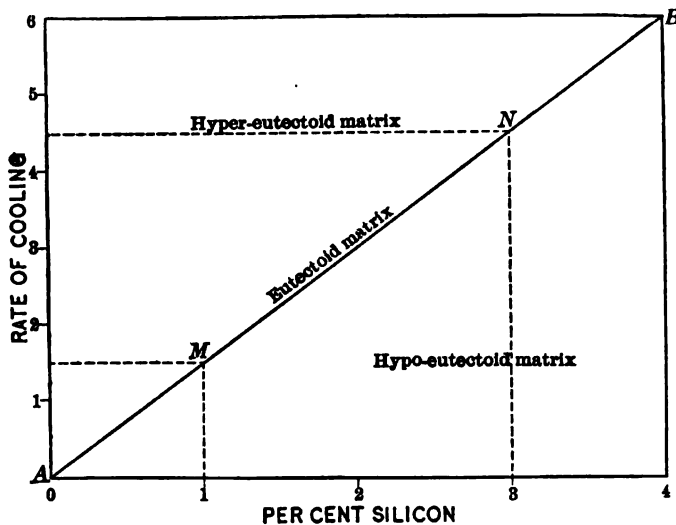


Fig. 362. — Influence of silicon content and of rate of cooling in determining the character of the matrix of cast iron.

reaching that line, which in pure iron-carbon alloys corresponds to a temperature of 1130 deg. C., it solidifies as an austenite-cementite eutectic containing *EG* (47.7 per cent) of austenite and *GF* (52.3 per cent) of cementite as later explained. On cooling from the solidus to the eutectoid line *HL* or Ar_1 point, at about 700 deg. C., the eutectic austenite rejects cementite (pro-eutectoid cementite) until it reaches the eutectoid composition (0.85 per cent of C or 12.75 per cent of Fe_3C). The pro-eutectoid cementite thus formed joins the eutectic cementite and is represented by the triangle *GIK* in the diagram. Clearly *IL* represents the total free cementite in the alloy when it reaches its eutectoid point. On cooling through this point the remaining austenite, now of eutectoid composition, breaks up into ferrite and cementite to form pearlite, a constituent which contains about 12.75 per cent of cementite (*OI* in the diagram) and 87.25 per cent of ferrite (*HO* in the diagram). Finally, then, the completely cooled alloy contains *ND* per cent of cementite of eutectic origin, *MN* per cent of cementite of pro-eutectoid origin, *PM* per cent of eutectoid cementite and *CP* per cent of ferrite. The eutectic and pro-eutectoid cementite known

collectively as “free” or “excess” cementite (MD) are so merged that they cannot be distinguished from each other, while the eutectoid cementite exists as a distinct constituent of pearlite. In the diagram PD represents the total cementite (free and eutectoid) in the alloy and CP the ferrite, that is its ultimate structural composition.

Solidification of Hyper-Eutectic Cast Iron. — The mechanism of the solidification of hyper-eutectic cast iron and of its subsequent transformation on slow cooling may be represented graphically, as shown in Figure 364. It is assumed in this diagram that no graphitic carbon is formed.

On reaching its liquidus, EF , in the vicinity of 1,200 deg. C. in the case of a pure alloy containing 5 per cent of carbon, cementite begins to form, and its formation continues to the solidus line, as indicated by the triangle FGH . On reaching the solidus (1130 deg. C.) the molten portion of the alloy has the eutectic composition (4.30 per cent of carbon), and it solidifies as an austenite-cementite eutectic, IG , containing IK per cent of austenite and KG per cent of cementite. This is in accordance with the solidification of the molten solution of any two metals capable of forming a eutectic alloy as explained in Chapters XXV and XXVI. On cooling from its solidus to its eutectoid or Ar_1 point (700 deg. C.) the eutectic austenite rejects cementite, as indicated by the triangle KQV , until, on reaching the eutectoid point, it is of eutectoid composition, and is converted into pearlite containing LM per cent of ferrite and MQ per cent of cementite. The alloy will finally consist of UD per cent of pro-eutectic cementite, TU per cent of eutectic cementite, ST per cent of pro-eutectoid cementite, RS per cent of eutectoid cementite, and CR per cent of ferrite. The pro-eutectic, eutectic, and pro-eutectoid cementites are merged, and cannot be distinguished from each other under the microscope. Their sum, SD , constitutes the free cementite of the alloy. The eutectoid cementite, RS , on the contrary, remains intimately associated with the ferrite to form the constituent pearlite, represented by CS in the diagram. RD represents the total percentage of cementite in the alloy.

Solidification of Hypo-Eutectic Cast Iron. — The mechanism of the solidification of hypo-eutectic alloys may likewise be graphically represented as shown in Figure 365. On reaching its liquidus, EF , pro-eutectic austenite containing 1.70 per cent of carbon begins to form. Assuming the cast iron to contain 3.50 per cent of carbon, its temperature would then be in the vicinity of 1225 deg. C. In cooling from the liquidus to the solidus or eutectic temperature, GK , austenite continues to form, the percentage of that constituent solidifying between the liquidus and the solidus being represented by the triangle EGH . On reaching the eutectic temperature, the liquid portion of the alloy has reached the eutectic composition and now solidifies as an austenite-cementite eutectic, HK , containing HI per cent of austenite and IK per cent of cementite following in this the behavior of all binary alloys in which a eutectic alloy is formed (Chapters XXV and XXVI). On cooling from the eutectic to the eutectoid or Ar_1 temperature, both the pro-eutectic and the eutectic austenite reject cementite, as indicated by the triangle IMN . At the eutectoid temperature, LO , the remaining austenite is of eutectoid composition and is transformed into pearlite, LM , containing LT per cent of ferrite and TM per cent of cementite. Below the eutectoid temperature, therefore, the cast iron consists of CR per cent of pearlite and RD per cent of free cementite, the pearlite containing CQ per cent of ferrite and QR per cent of cementite, and the free cementite RS per cent of cementite of eutectic

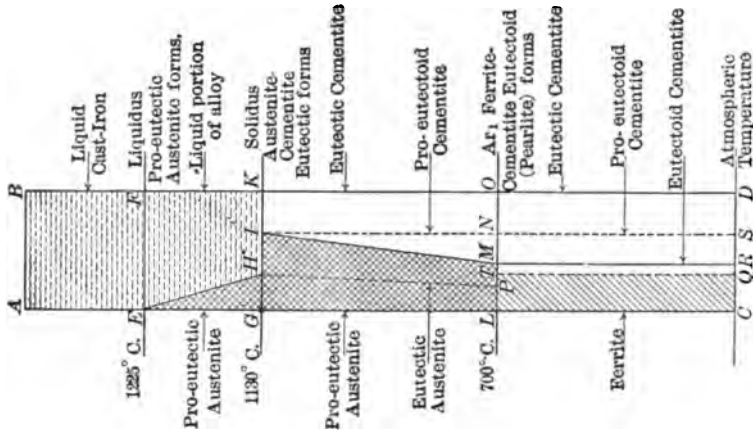


Fig. 363. — Diagram illustrating the mechanism of the solidification of eutectic cast iron.

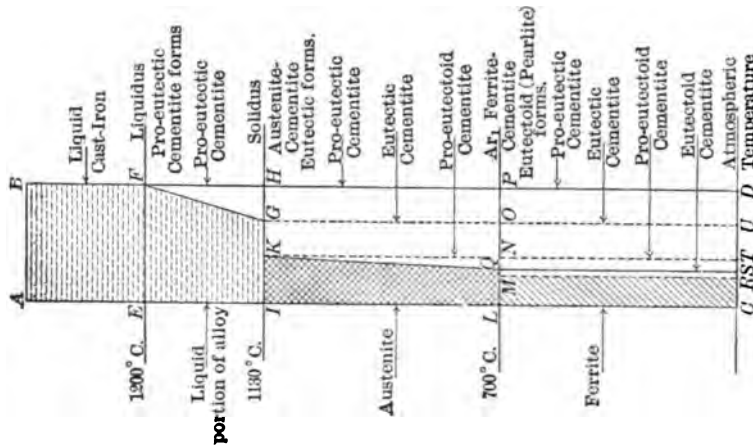


Fig. 364. — Diagram illustrating the mechanism of the solidification of hyper-eutectic cast iron.

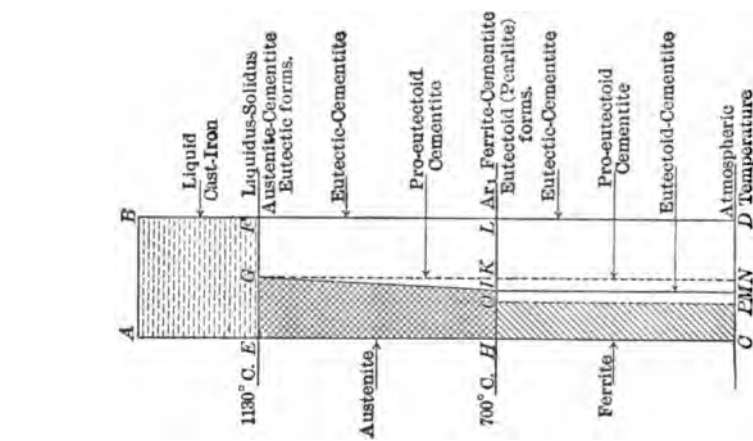


Fig. 365. — Diagram illustrating the mechanism of the solidification of hypo-eutectic cast iron.

origin, and *SD* per cent of cementite of pro-eutectoid origin. *QD* evidently represents the total cementite in the alloy.

The Graphitizing of Cementite. — It is well known as more fully explained in Chapters XXIV and XXVI that cementite readily breaks up into iron (ferrite) and graphite when heated to a sufficiently high temperature, and it is likewise well known that the higher the temperature the more easily does this dissociation take place, and that silicon also promotes it. Bearing in mind the influence of temperature on the graphitization of cementite, we are justified in assuming that the higher the temperature at which cementite forms the more readily will it be converted into ferrite and graphite on subsequent cooling. It follows from the foregoing assumption that the graphitization of the cementite formed in iron-carbon alloys during and below their solidification will take place in the following order with increasing difficulty: (1) graphitization of pro-eutectic cementite, (2) graphitization of eutectic cementite, (3) graphitization of pro-eutectoid cementite, and (4) graphitization of eutectoid cementite.

Graphitizing of Hyper-Eutectic Alloys. — In hyper-eutectic alloys pro-eutectic cementite forms as soon as the alloy begins to solidify and keeps on forming to the eutectic temperature. At such high temperature the dissociation tendency is so great that graphite very readily forms, even in the absence of silicon and during relatively rapid cooling. If time be given, the graphite resulting from the dissociation of pro-eutectic cementite rises to the surface of the still liquid bath, when it is known as "kish." Upon reaching the eutectic temperature, eutectic cementite forms, which easily breaks up into iron and graphite if the cooling be sufficiently slow, its graphitization being assisted by the presence of *nuclei* of pro-eutectic graphite. In cooling from the eutectic to the eutectoid temperature pro-eutectoid cementite is expelled by the austenite. The graphitization of pro-eutectoid cementite, however, proceeds with less readiness because of the relatively low temperature now prevailing, although assisted by the presence of many *nuclei* of pro-eutectic and eutectic graphite. A large percentage of silicon and very slow cooling would of course promote it. If some of the pro-eutectoid cementite fails to be graphitized the resulting cast iron will necessarily have a hyper-eutectoid matrix and will probably be mottled. Upon reaching the eutectoid temperature eutectoid cementite is formed, but its graphitization, although greatly assisted by the presence of much graphite, will require, at least to be complete, very slow cooling and the presence of considerable silicon. It is, of course, evident that if some pro-eutectoid cementite has escaped graphitization none of the eutectoid cementite will graphitize, since the dissociation of cementite becomes more difficult as the temperature is lowered. In case the graphitization of eutectoid cementite is complete, a rare instance, the resulting cast iron has a pure, or rather carbonless, ferrite matrix. If it is incomplete the matrix will be hypo-eutectoid and the cast iron belong to one of the foundry grades.

Graphitizing of Eutectic Alloys. — On reaching the solidification temperature eutectic cementite is formed, which breaks up quite readily into ferrite and graphite unless prevented from doing so through rapid cooling. On cooling from the eutectic to the eutectoid temperature pro-eutectoid cementite forms, the graphitization of which is promoted by the presence of *nuclei* of eutectic graphite but opposed by the lower temperature now prevailing. It may, however, be complete in the presence of sufficient silicon. If it remains incomplete the cast iron will have a hyper-eutectoid matrix. The graphitization of the eutectoid cementite formed at the eutectoid

temperature is much less readily brought about, being now opposed by the low temperature of the metal. It will generally remain incomplete and the resulting cast iron will have a hypo-eutectoid matrix.

Graphitizing of Hypo-Eutectic Alloys. — In hypo-eutectic alloys when solidification begins austenite is formed and at the eutectic temperature eutectic cementite falls out of solution. This cementite undergoes graphitization quite readily because of the high temperature at which it forms. On cooling from the eutectic to the eutectoid temperature pro-eutectoid cementite is rejected by austenite, and its graphitization proceeds the more slowly that it is not now assisted by pre-existing *nuclei* of graphite to the same extent as eutectic and hyper-eutectic alloys. The eutectoid cementite is graphitized with difficulty because of low temperature and of relatively little pre-existing graphite. If the graphitization of pro-eutectoid cementite remains incomplete the cast iron will have a hyper-eutectoid matrix, while in case of complete graphitization of the pro-eutectoid cementite but incomplete graphitization of eutectoid cementite it will have a hypo-eutectoid matrix. In case of complete graphitization of the pro-eutectoid cementite and of no graphitization at all of the eutectoid cementite the cast iron would have a eutectoid matrix.

CHAPTER XXIII

IMPURITIES IN CAST IRON

In the preceding chapter cast iron has been considered as a pure alloy of iron and carbon, but like steel, commercial cast iron always contains varying proportions of silicon, manganese, phosphorus, and sulphur, and we should now examine the influence of these impurities on its structure and consequently on its properties.

Silicon in Cast Iron. — Cast iron seldom contains less than 0.50 per cent silicon and frequently as much as 3 or 3.50 per cent. As in the case of steel this silicon probably combines with some of the iron to form the silicide of iron, FeSi , which is then dissolved in the balance of the iron. The ferrite of cast iron, therefore, always holds a considerable amount of silicon or rather of the silicide FeSi in solution. It has been seen that silicon produces exactly three times its own weight of FeSi ; cast iron with 2 per cent of silicon, for instance, will contain 6 per cent of FeSi dissolved in its ferrite. The influence of silicon on the properties of cast iron is very important chiefly through its promoting the formation of graphitic carbon and, therefore, increasing the softness and, if carried too far, decreasing the strength of cast iron. It is why foundrymen often speak of silicon as a "softener." The influence of silicon in causing the decomposition of the carbide Fe_3C is ascribed by Stead, Hatfield, and others to the presence of some silicon in the carbide which is thereby rendered less stable. That silicon increases fluidity while decreasing shrinkage and chill is also well known.

The influence of silicon to decrease the percentage of carbon in the iron-carbon eutectic has been considered in the preceding chapter.

The occurrence of varying amounts of silicon in cast iron cannot be detected under the microscope, unless indirectly and roughly through the presence of more or less graphitic carbon. It is probably true, however, that under otherwise similar conditions, the more silicon present in ferrite the slower the etching of that constituent. The ferrite of cast iron with hypo-eutectoid matrix, for instance, possibly because of its greater silicon content, often remains brilliant after the usual deep etching treatment which would color decidedly some of the grains of the ferrite of wrought iron or of low carbon steel.

Sulphur in Cast Iron. — Cast-iron castings of good quality should not contain more than 0.1 per cent of sulphur while but a trace of that element may be present. In the manufacture of chilled castings, however, as much as 0.2 per cent sulphur is sometimes allowed. It has been explained in Chapter IX that because of the great affinity of manganese for sulphur these two elements readily combine to form the manganese sulphide MnS , each part by weight of sulphur giving rise to the formation of approximately $2\frac{1}{2}$ parts of MnS . Cast iron with 0.05 per cent sulphur, for instance, would contain about 0.125 per cent of MnS . As in the case of steel this

sulphide occurs in the form of rounded particles of a dove gray or slate color embedded in the metallic matrix (Fig. 366). Should there not be enough manganese present to combine with all the sulphur, the remaining sulphur would unite with iron to form the sulphide FeS which would occur as rounded yellow areas. It should be noted, however, that since it requires less than 2 parts by weight of manganese to combine with 1 part of sulphur, when cast iron contains twice as much manganese as it does sulphur no iron sulphide can be formed, theoretically at least. Since it is seldom that cast iron does not contain a considerably greater proportion of manganese the occurrence of FeS in cast iron should be rare.

The influence of sulphur in opposing the formation of graphitic carbon has already been mentioned; it may consequently be said to harden cast iron. Hatfield believes

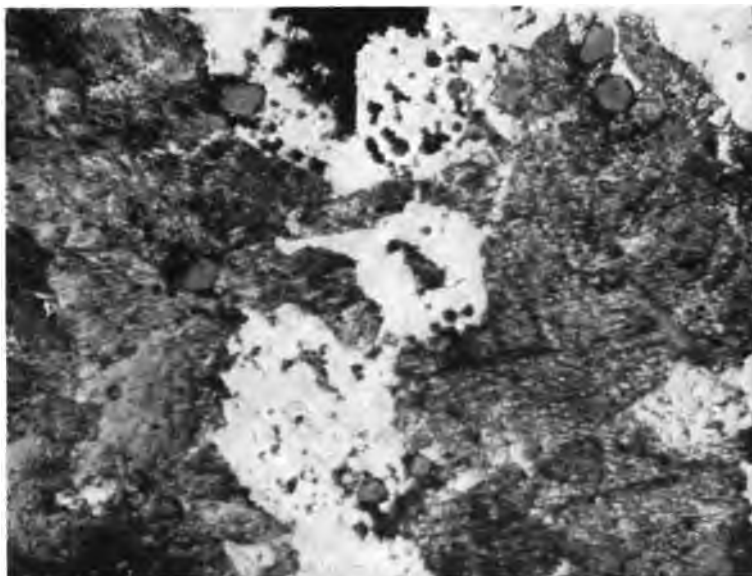


Fig. 366. — Partially malleablized cast iron. Magnified 670 diameters. Sulphur about 0.2 per cent, manganese 0.50 per cent. (C. C. Buck, Correspondent Course student.)

that this influence of sulphur is due to the presence of some sulphide of iron dissolved in the iron carbide and increasing its stability. It has also a well-known influence in increasing the depth of “chill” in solidifying cast iron against a metal wall, that is the thickness of metal free from graphitic carbon produced by the cooling action of that wall. Its other influences are harmful as it increases shrinkage, causes the molten metal to be sluggish, and induces unsoundness.

Manganese in Cast Iron. — Special cast irons are made, known as spiegeleisen, ferro-manganese, etc., containing very large proportions of manganese, but in ordinary castings the amount of manganese seldom exceeds 2 per cent and may be as low as 0.10 per cent. It has been shown in Chapter IX that when manganese is present in these relatively small proportions it first combines with sulphur to form the sulphide MnS , and then with carbon to form the carbide Mn_3C , this carbide uniting with the

carbide Fe_3C to form cementite. The cementite of cast iron, therefore, like that of steel nearly always contains some Mn_3C . Since iron and manganese, however, have nearly the same atomic weights it remains true that to obtain the percentage of cementite in any commercial iron-carbon alloy it suffices to multiply its percentage of combined carbon by fifteen.

The influence of manganese in opposing the formation of graphitic carbon has already been noted. It is explained by some on the ground that the carbide Mn_3C is more stable than Fe_3C . Like sulphur manganese is a hardener, its presence in large proportions increasing the difficulty of machining castings. It promotes the absorption of carbon by iron. Some believe that it increases shrinkage and that while it has no marked influence on the depth of the chill it increases its hardness.



Fig. 367. — Alloy of iron and phosphorus. Phosphorus 1.8 per cent. Magnified 350 diameters. (Stead.)



Fig. 368. — Alloy of iron and phosphorus. Phosphorus 8 per cent. Magnified 250 diameters. (Stead.)

Phosphorus in Cast Iron. — It has been explained in Chapter IX that when phosphorus occurs in very small quantities as it does in steel, the totality of it probably forms the phosphide Fe_3P , which is then dissolved by the iron. In cast iron, however, because of the frequent presence of a considerable proportion of phosphorus and of a larger proportion of carbon this element assumes another condition. The occurrence of phosphorus in cast iron was first studied and described by Stead. The results of his important investigations are briefly summarized below:

(1) When phosphorus is alloyed with carbonless iron in amounts varying from traces to 1.70 per cent, it forms a phosphide corresponding to the formula Fe_3P , which is held in solid solution by the iron. All the metals used commercially, such as wrought iron and steels containing very little carbon, may be included in this class. They consist essentially of polyhedral grains of ferrite holding Fe_3P in solution.

(2) When the metal contains from 1.70 to 10.2 per cent phosphorus it consists of a saturated solution of Fe_3P in iron (1.70 per cent P) and of a eutectic alloy contain-

ing about 10.2 per cent P and made up of about 61 per cent Fe_3P and 39 per cent of the saturated solution of Fe_3P in iron. To account readily for this structure and that of the following groups, it is only necessary to consider these metals as alloys of two constituents: one the phosphide Fe_3P , and the other a saturated solution of Fe_3P in iron. It is well known that a certain class of binary alloys when solidifying give rise to the formation of a eutectic alloy, that is, of a mechanical mixture made up in definite proportions, of extremely small plates alternately of one and the other constituents, the balance of the mass consisting of that constituent which is present in excess over the amount required to form the eutectic alloy. It is precisely what happens in the case of iron containing over 1.70 per cent phosphorus. The formation of eutectic alloys will be further described in Chapter XXV.

Figures 367, 368, and 369 illustrate the structure of iron containing respectively 1.8, 8, and 10.2 per cent phosphorus. The mottled constituent made up of two struc-



Fig. 369. — Alloy of iron and phosphorus. Phosphorus 10.2 per cent. Magnified 350 diameters. (Stead.)



Fig. 370. — Alloy of iron and phosphorus. Phosphorus 11.07 per cent. Magnified 60 diameters. (Stead.)

tural elements in close juxtaposition corresponds in every case to the phosphide eutectic. The background of Figure 367 and the clear regions of Figure 368 are composed of the solid saturated solution, while Figure 369 is composed entirely of the eutectic alloy.

(3) When the iron contains from 10.2 per cent to 15.58 per cent phosphorus it is composed of crystals of Fe_3P surrounded by the eutectic mixture just described, as illustrated in Figure 370, in which the white angular areas represent Fe_3P and the background the eutectic alloy.

When carbon is present in considerable quantity as in cast iron, the phosphorus held in solution by the iron in the absence of carbon is thrown out of solution almost completely and a ternary eutectic formed (Stead, Wüst, Gørens) containing according to Stead 91.19 per cent iron, 6.89 per cent phosphorus, and 1.92 per cent carbon, its proximate constituents being iron carbide (Fe_3C), iron phosphide (Fe_3P),

and iron (ferrite) containing a little phosphorus in solution. After heat tinting the constituents of the ternary eutectic are readily distinguishable, the iron carbide being colored red, the iron phosphide purple, and the ferrite containing some phosphorus

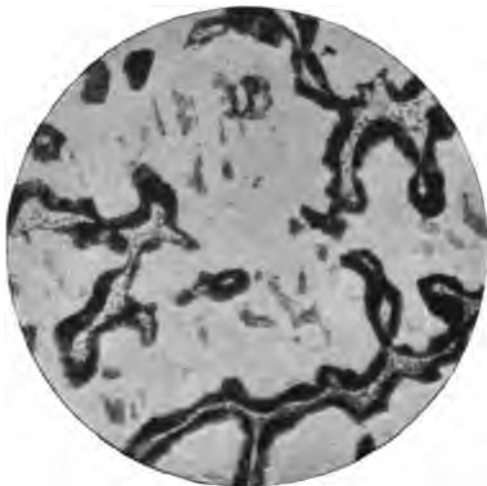


Fig. 371. — Alloy of iron, phosphorus, and carbon. Phosphorus 1.74 per cent, carbon 0.18 per cent. Magnified 60 diameters. (Stead.)



Fig. 372. — Alloy of iron, phosphorus, and carbon. Phosphorus 1.70 per cent, carbon 0.71 per cent. Magnified 250 diameters. (Stead.)

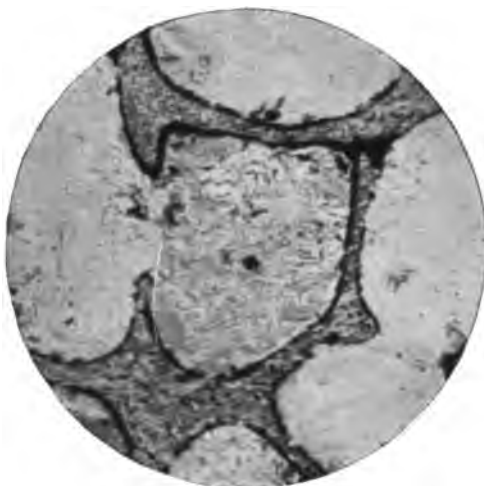


Fig. 373. — Alloy of iron, phosphorus, and carbon. Phosphorus 1.70 per cent, carbon 1.40 per cent. Magnified 250 diameters. (Stead.)

in solution, white. While such is the character of the phosphide eutectic in white and mottled cast iron, Stead writes that in very gray phosphoretic metals the carbon diffuses out of it and a binary eutectic of Fe_3P and iron containing in solution

a little phosphorus is formed. For this binary phosphide eutectic of gray cast iron first described by Stead in 1900 the author proposed the name of "steadite." It contains according to Stead about 10 per cent phosphorus and 90 per cent iron.

The structures of some iron alloys containing 1.70 per cent phosphorus and increasing proportions of carbon are illustrated in Figures 371 to 373. The increasing proportion of phosphorus thrown out of solution as a eutectic will be noted.

It will be obvious from the above description of the behavior of phosphorus that in cast iron, because of the presence of a large amount of carbon, nearly the whole of the phosphorus is liberated from its solution with iron and caused to occur as a ternary eutectic in white and mottled cast iron and as a binary eutectic or steadite in gray cast iron, even if the metal contains less than the necessary amount of phosphorus needed to saturate the iron, namely 1.70 per cent. Indeed so marked is this action of carbon that Stead tells us that in steel containing but 0.1 per cent phosphorus a portion of it is liable to be thrown out of solution in the presence of 0.90 per cent carbon.

To sum up, the phosphorus in ordinary steels occurs chiefly and probably altogether as the phosphide Fe_3P dissolved in iron while in cast iron it occurs chiefly if not entirely as a eutectic. While Stead writes that the whole of the phosphorus is not liberated from solution even in the presence of much carbon, the amount retained in solution in the presence of some 3 per cent or more carbon is apparently very small and it may probably be assumed for all practical purposes that in cast iron the whole of the phosphorus is present as a eutectic, for Stead says that the phosphide eutectic may be detected in cast iron containing as little as 0.03 per cent phosphorus. The structure of gray phosphoretic cast iron is illustrated in Figures 374 to 377. The various constituents, graphite, pearlite, free ferrite, and steadite are easily distinguishable as follows: dark plates, graphite; dark, rounded constituent, pearlite; white, structureless, ferrite; white, mottled (dotted), steadite. The structure of the phosphide eutectic is shown more highly magnified in Figure 375. The matrix of the cast iron illustrated in Figures 374 and 375 is free from combined carbon, consisting, therefore, exclusively of ferrite and steadite; in Figure 376 the matrix contains both considerable pearlite and free ferrite; the cast iron shown in Figure 377 has a eutectoid matrix.

Stead recommends heat tinting as a suitable treatment for bringing out the phosphide eutectic, especially in white cast iron when there is danger of confounding it with cementite. The heat-tinting method of Stead has been described in Chapter II.

Stead explains as follows the fact that a relatively high proportion of phosphorus in cast iron does not produce extreme brittleness.

"The reason why phosphoretic pig irons are not more brittle than they are is because the eutectic separates into isolated segregations, and does not form continuous cells round the crystalline grains. When the phosphorus does not exceed 1.7 per cent the metal is comparatively strong, but an addition of 0.3 per cent reduces the strength materially, the reason of which is that the eutectic brittle areas in metal with 2 per cent phosphorus approach each other closely, leaving less of the strong ground mass intervening."

Phosphorus has no marked influence upon the condition in which carbon occurs in cast iron but it increases the fluidity of the metal probably because of the formation of a large quantity of fusible and fluid phosphide eutectic.

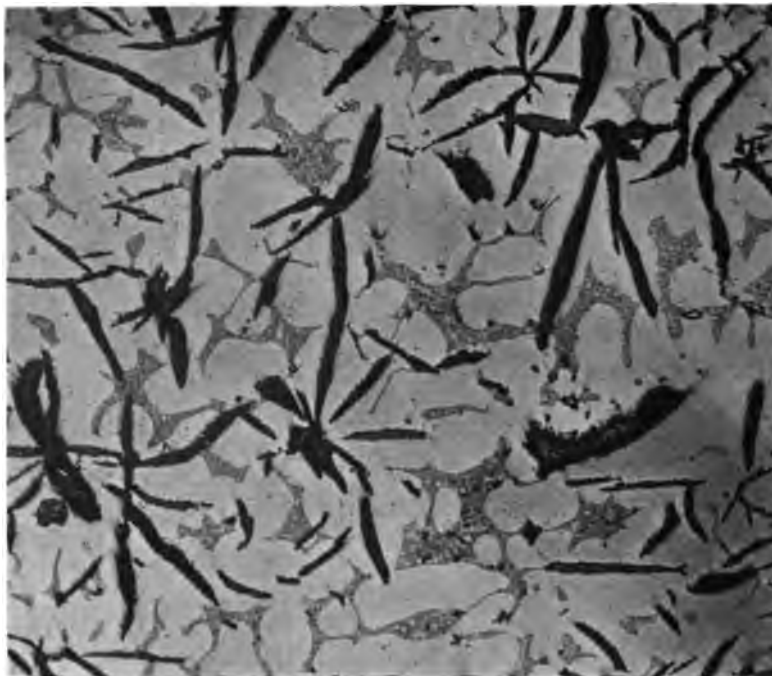


Fig. 374. — Cast iron. Graphitic carbon 3.06 per cent. Combined carbon 0.08 per cent. Phosphorus 1.36 per cent. Magnified 100 diameters. (F. H. Franklin of Saunders and Franklin.)

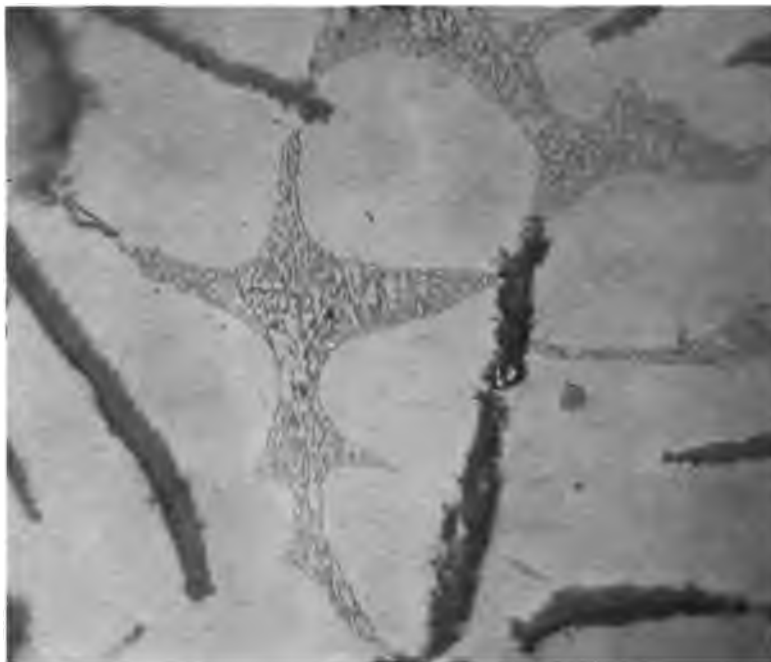


Fig. 375. — Same as Fig. 374 but magnified 425 diameters. (F. H. Franklin of Saunders and Franklin.)



Fig. 376. — Cast iron. Magnified 100 diameters. Graphite, ferrite, pearlite, and steadite. (Boylston.)

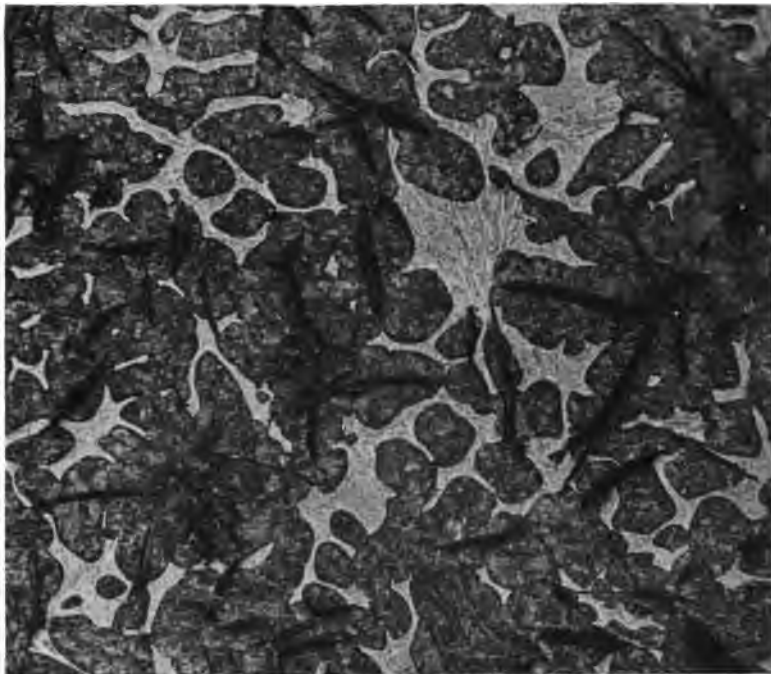


Fig. 377. — Cast iron. Eutectoid matrix. Phosphorus 1.36 per cent. Magnified 100 diameters. (F. H. Franklin of Saunders and Franklin.)

Critical Points of Cast Iron Containing Phosphorus. — H. I. Coe has published the interesting and significant cooling curves of cast iron containing increasing proportions of phosphorus reproduced in Figure 378. In the six samples of cast iron involved the percentages of phosphorus were respectively 0.09, 0.53, 1.01, 1.23, 2.16, and 2.90. The two upper points correspond to the solidification of the iron-carbon alloys, as explained in Chapters XXV and XXVI, the third point to the solidification of the phosphide eutectic¹ and the fourth to the recalescence point (pearlite formation). It is to be inferred from these curves that as phosphorus increases (*a*) the melting-point of the alloy is lowered, (*b*) the intensity of the third point increases, (*c*) the position of the third point is slightly raised, and (*d*) the position of the point of recalescence remains practically unaffected.

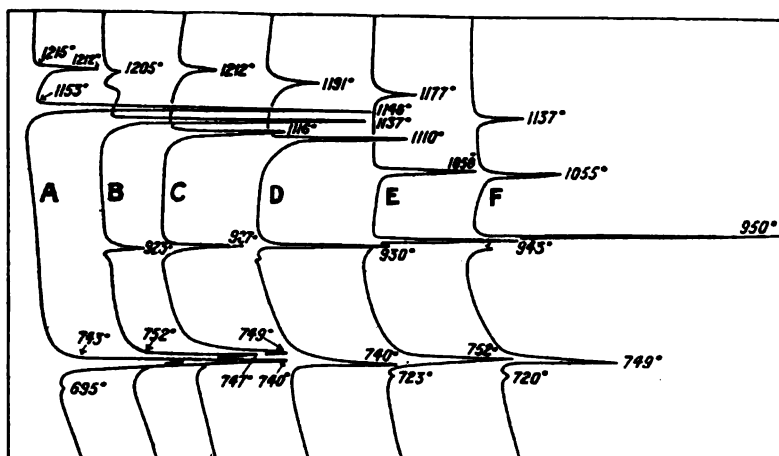


Fig. 378. — Cooling curves of cast-iron samples containing increasing percentages of phosphorus. (H. I. Coe.)

Structural Composition of Phosphoretic Cast Iron. — Since the presence of 10.2 per cent phosphorus causes the production of 100 per cent steadite it follows that the phosphorus in cast iron gives rise to the formation of approximately 10 times its own weight of steadite.

In calculating the structural composition of cast iron, therefore, the amount of phosphorus present must be considered as it may very materially lower the percentage of combined carbon needed to convert its matrix into pearlite. Bearing in mind that cast iron to be free from both free ferrite and free cementite must contain ferrite and cementite in the proportion of seven to one the following relation will indicate the needed amount of combined carbon:

$$\begin{aligned} \text{Ferrite} &= 100 - G - 10\text{Ph} - 15C = 7 \times 15C = 105C \\ &\quad \downarrow \\ &\quad \text{cementite} \\ \text{or } 100 - G - 10\text{Ph} - 120C &= 0 \end{aligned}$$

¹ Stead indicates 980 to 1000 deg. C. as the solidification point of the phosphide eutectic.

in which G, C, and Ph represent respectively the percentage of graphite, combined carbon, and phosphorus, 15C representing, of course, the proportion of cementite and 10Ph that of steadite.

If the first term of the above equation is greater than 0 the metal will contain free ferrite, i.e. its matrix will be hypo-eutectoid; if it is smaller than 0 it will contain free cementite, i.e. its matrix will be hyper-eutectoid.

In the presence of 3 per cent of graphite and 1 per cent phosphorus, for instance, the percentage of combined carbon needed to produce a eutectoid matrix will readily be obtained in solving the equation

$$100 - 3 - 10 - 120C = 0$$

which calls for 0.73 per cent combined carbon. Less combined carbon would produce free ferrite while more would cause the formation of free cementite.

In calculating the structural composition of any phosphorectic cast iron of known percentage of phosphorus, graphite, and combined carbon, it should first be ascertained therefore whether its matrix will be hypo- or hyper-eutectoid. Let us assume, for instance, a cast iron containing 1.50 per cent phosphorus, 3.25 per cent graphite, and 0.40 per cent combined carbon. Since $100 - 3.25 - 15 - 120 \times 0.40$ is greater than 0 the matrix of the iron will be hypo-eutectoid, that is the metal will contain free ferrite. The following equations will then permit the ready calculation of its structural composition.

$$(1) P + F + S + G = 100$$

$$(2) P = 120C$$

$$(3) S = 10Ph$$

which give

Pearlite (P)	= 48.00 per cent
Free ferrite (F)	= 33.75 " "
Steadite (S)	= 15.00 " "
Graphite (G)	= 3.25 " "
	<u>100.00</u>

Taking another example, a cast iron containing 2 per cent graphite, 1.50 per cent combined carbon, and 0.75 per cent of phosphorus, since $100 - 2 - 7.50 - 120 \times 1.50$ is less than 0, the iron will contain free cementite. Its structural composition will be obtained by solving the equations

$$(1) P + Cm + S + G = 100$$

$$(2) P = \frac{2}{3}(100 - 15C - 10Ph - G)$$

$$(3) S = 10Ph$$

which give

Pearlite (P)	= 77.78 per cent
Free cementite (Cm)	= 12.72 " "
Steadite (S)	= 7.50 " "
Graphite (G)	= 2.00 " "
	<u>100.00</u>

Chemical vs. Structural Composition. — It will now be instructive to compare the chemical composition of cast iron both ultimate and proximate with its structural

composition. To that effect let us assume a cast iron of the following ultimate chemical composition:

Graphitic carbon	3.00 per cent
Combined carbon	0.50 “ “
Silicon	2.00 “ “
Phosphorus	1.50 “ “
Manganese	0.40 “ “
Sulphur	0.02 “ “
Iron (by difference)	92.58 “ “
	<u>100.00</u>

In view of the foregoing considerations the following proximate compounds will be formed:

- (1) 0.02 per cent S will produce about 0.05 per cent MnS.
- (2) 0.05 per cent MnS contains about 0.03 per cent Mn.
- (3) This leaves $0.40 - 0.03 = 0.37$ per cent Mn in excess to combine with carbon.
- (4) 0.37 per cent Mn will form 0.39 per cent Mn_3C .
- (5) 0.39 per cent Mn_3C contains about 0.02 per cent carbon.
- (6) This leaves $0.50 - 0.02 = 0.48$ per cent carbon to combine with iron.
- (7) 0.48 per cent carbon will form 7.20 per cent Fe_3C .
- (8) 1.50 per cent phosphorus will form 9.63 per cent Fe_3P .
- (9) 2.00 per cent silicon will form 6.00 per cent FeSi.

The proximate chemical analysis of the cast iron considered will consequently be:

Graphitic carbon	3.00 per cent
Fe_3C	7.20 “ “
Mn_3C	0.39 “ “
Fe_3P	9.63 “ “
FeSi	6.00 “ “
MnS	0.05 “ “
Iron (by difference)	73.73 “ “
	<u>100.00</u>

Knowing the proximate chemical constituents the structural composition can be readily calculated. The Fe_3C and Mn_3C form the cementite, hence the cast iron contains $7.20 + 0.39 = 7.59$ per cent cementite. The whole of this cementite, since the iron evidently has an hypo-eutectoid matrix, will combine with ferrite in the proportion of 7 to 1 to form pearlite, hence the cast iron will contain $7.59 \times 8 = 60.72$ per cent pearlite; 1.50 per cent phosphorus means 15.00 per cent of steadite; the 6.00 per cent of FeSi will be dissolved in the ferrite while the small quantity of MnS will occur as independent minute particles. The structural composition will therefore be:

Pearlite (P)	= 60.72 per cent
Free ferrite (F) (by difference)	= 21.23 “ “
Steadite (S)	= 15.00 “ “
Graphite (G)	= 3.00 “ “
MnS	= 0.05 “ “
	<u>100.00</u>

The quicker method for the calculation of the structural composition of cast iron given in foregoing pages, and in which the presence of manganese, silicon, and sulphur is ignored would have given:

Pearlite (P)	60.00
Free ferrite (F)	22.00
Steadite (S)	15.00
Graphite (G)	3.00
	<hr/> 100.00

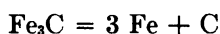
For practical purposes these values are identical to those obtained from a knowledge of the complete analysis of the iron.

Other Impurities. — Nickel in appreciable quantity seldom occurs in cast iron. It is believed to form a solid solution with ferrite and to promote the formation of graphitic carbon. Vanadium probably strengthens cast iron, an influence which is explained by W. H. Hatfield on the ground that the bulk of the vanadium crystallizes with the iron carbide which is thereby rendered more stable. J. E. Johnson has recently contended that oxygen strengthens and otherwise improves cast iron while Moldenke blames oxygen for many of the ailments from which it occasionally suffers. Many doubt the presence of any appreciable amount of oxygen in cast iron.

CHAPTER XXIV

MALLEABLE CAST IRON

Graphitizing of Cementite. — The unstability of cementite has already been alluded to. It has been mentioned that the prolonged annealing of high carbon steel above its critical range was always likely to result in the formation of some graphitic carbon through the dissociation of the unstable cementite according to the reaction:



The graphitic carbon formed in this way is often called, according to Ledebur, "temper" carbon to distinguish it from the graphite formed during the solidification of cast iron. This breaking up of cementite into ferrite and graphite takes place the more readily (1) the more combined carbon in the metal, (2) the higher the temperature, (3) the longer the exposure to a high temperature, (4) the more silicon and the less manganese and sulphur present. The influence of a large amount of combined carbon in promoting the graphitizing of cementite is made evident by the facts (1) that iron-carbon alloys containing less than some 0.50 per cent carbon cannot be made graphitic under the most favorable annealing conditions even when containing much silicon, (2) that in steel containing in the vicinity of 1 per cent carbon the graphitizing proceeds very slowly and remains partial, and (3) that in alloys containing 2.50 per cent or more of combined carbon and a sufficient amount of silicon the conversion of cementite into iron and graphite takes place readily and can be carried to completion, combined carbon disappearing altogether. The influence of temperature and time upon the dissociation of cementite was to be expected. Evidences will be presented in Chapter XXVI to show that the higher the temperature at which cementite forms the more readily is it converted into iron and graphitic carbon, during solidification and subsequent cooling. The influence of silicon in graphitizing cementite could likewise have been anticipated because of its well-known power to cause the formation of graphitic carbon during and below solidification. It will be argued in Chapter XXVI that the formation of graphite during solidification always results from the dissociation of cementite, that is, that cementite (Fe_3C) always forms first but being very unstable readily breaks up into iron and graphite, its dissociation being promoted (1) by slow cooling and (2) by the presence of silicon.

The conversion of combined carbon into graphitic or rather temper carbon finds an important industrial application in the manufacture of so-called malleable cast-iron castings, also termed "malleable castings," "malleable cast iron," and even "malleable" pronounced "mallable."

The metallography of these castings should now be considered.

Malleable Cast-Iron Castings. — The adjective "malleable" always used in describing these castings is misleading for it suggests a malleability, and other proper-

ties akin to those of steels, which malleable castings are far from possessing. By malleability the metallurgist always understands that property which makes it possible to convert a metallic mass into commercial shapes by rolling, hammering, etc., and such degree of malleability is not present in malleable cast iron. It is why in the author's opinion this product should continue to be classified as cast iron in spite of the arguments recently presented to classify it as steel on the ground that it is more malleable than ordinary cast iron. The manufacture of malleable cast-iron castings consists in subjecting to a long annealing treatment cast-iron castings of suitable composition whereby some of the carbon may be expelled by oxidation while most if not the whole of the remaining is converted into graphite (temper carbon). The various factors influencing this operation will be briefly described.

Original Castings. — The castings to be subjected to the malleablizing treatment are often called "hard" castings because they are invariably made of white cast iron and are therefore very hard and brittle. The reason why the original castings must be made of white cast iron will be obvious if it be considered that the malleability to be imparted to these castings is to result chiefly, and in some cases altogether, from a conversion of combined carbon into temper carbon as explained above. Any graphite particle existing in the casting will be unaffected by the annealing treatment and will be a source of weakness in the finished casting. Clearly, therefore, the hard castings should be free from graphitic carbon. As to the amount of carbon that should be present, theoretical considerations lead us to conclude that the less carbon the more ductile should be the castings after thorough malleablizing, for, after all, the particles of temper carbon while much less injurious than the hard brittle cementite from which they are derived are nevertheless a source of weakness chiefly because of their breaking up the continuity of the metallic mass. Again a smaller proportion of carbon necessarily means a shorter annealing operation. The desirability of low carbon content in cast-iron castings to be malleablized is universally recognized and it is partly why a large proportion of these castings are made in the "air" furnace or open hearth furnace, as by their use the percentage of carbon can be lowered. On the other hand, as already mentioned, if the proportion of combined carbon be small the graphitizing takes place with greater difficulty. These considerations point to the existence of a lower as well as of an upper limit for the carbon content of hard castings. In the majority of cases the percentage of carbon varies between 2.50 and 3.00 per cent. According to Moldenke it should not be lower than 2.75 per cent.

The beneficial action of silicon has been referred to; it greatly promotes the graphitizing of the cementite. It might seem then as if the more silicon in the hard casting the better at least up to some 2 or 3 per cent. Castings of white cast iron cannot be made, however, in the presence of much silicon since this element would cause the formation of graphitic carbon on solidification, even during quick cooling, and the casting would not be white. And since large castings will solidify more slowly than smaller ones it is evident that in large castings especially but a relatively small amount of silicon can be allowed. It is probably true that as much silicon should be introduced in the cast iron as will permit the making of white castings and this proportion of silicon will necessarily decrease as the size of the casting increases. In practise it is found to vary between 0.30 per cent in large castings (4 inches thick or more) and 1.25 per cent in very small castings for like solidification conditions and subsequent cooling. In the majority of cases the silicon content varies between 0.50 and

1 per cent.¹ Moldenke writes that the best all around percentage of silicon for general castings is 0.65. A. Lissner recommends 0.9 per cent silicon for castings one inch thick.

In Moldenke's opinion the manganese should not exceed 0.60 per cent as a larger amount is liable to cause trouble on annealing and difficulty in machining. Phosphorus according to the same authority should not exceed 0.225 per cent while sulphur should not exceed 0.07 and preferably not 0.05 per cent. These figures represent American practise only, in Europe cast-iron castings being malleablized containing considerably more sulphur and phosphorus.



Fig. 379. — Hard casting (white cast iron). Magnified 67 diameters. (Boylston.)

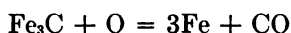
The structure of a hard casting of suitable composition for the malleablizing process is shown in Figure 379. It will be seen to be characteristic of the structure of white cast iron.

Annealing Operation. — The hard castings are placed in an annealing box and firmly packed in a suitable material. The boxes are then placed in the annealing furnaces and with their contents exposed to a desirable temperature for a suitable length of time. These various steps should be briefly considered.

Packing Materials. — The packing material affords a support for the castings while it may or may not play an important part in the process itself according to its being (1) oxidizing or (2) non-oxidizing. In his pioneer work, in 1722, Réaumur surrounded white cast iron with crushed iron oxide, the oxygen of which removed a large proportion of the carbon during the subsequent long annealing treatment at a high temperature. Given a sufficiently high temperature and sufficiently long exposure nearly the whole of the carbon could in this way be eliminated from small cast-

¹ According to A. Lissner doubling the sulphur reduces the speed of dissociation of the cementite 5 times while an increase of 0.8 per cent silicon doubles the speed. The restraining effect of 0.05 per cent sulphur is neutralized by an increase of 0.28 per cent silicon.

ings, a small amount of it only remaining as temper carbon. It will be evident that in the operation conducted in this way the oxidizing action of the packing is of more importance in producing malleability than the graphitizing of the cementite. The elimination of the carbon takes place through the well-known reaction between the iron oxide (from the packing) and the carbon in the steel,



the cementite in the center migrating towards the outside and being in turn acted upon by the oxygen of the packing material.

It will be evident that this elimination must necessarily proceed from the outside to the center, so that if one should interrupt the operation after a relatively short time he would find an increasing proportion of carbon from shell to center. The use of an oxidizing and therefore chemically active packing material was for a long time considered essential in the malleablizing process. Later investigations, however, showed that white cast iron could be made malleable solely through the conversion of combined into graphitic carbon with very little if any removal of the carbon and that an oxidizing packing was not therefore necessary. Inert packing such as sand and clay may be used and satisfactory malleable castings produced. It is customary, however, in American practise, to use oxidizing packings but to depend chiefly on the graphitizing of cementite brought about by annealing for the desired malleability and strength. Although realizing that an oxidizing substance as a packing material is not indispensable it is still preferred because of the apparent greater strength its use confers to the castings. The substances most used are powdered iron oxides in the shape of iron ore, mill scale, puddle cinder, "bull-dog," etc., and, according to Moldenke, the crushed flakes detached from the annealing pots themselves.

Annealing for Malleablizing. — The malleability imparted to white cast iron by annealing results from, as explained in the foregoing pages, (1) the hard brittle cementite being converted into minute rounded particles of soft graphitic (temper) carbon and (2) the burning of some carbon by the oxygen of the packing materials. If we depend chiefly upon the burning of the carbon for the desired malleability, so-called "white heart" castings are produced, while if the graphitizing of cementite is mainly sought, so-called "black heart" castings are obtained. The temperature and length of the annealing operation vary according to the kind of castings wanted.

The annealing operation is always conducted above the critical point $\text{Ac}_{3.2.1}$ of the white cast iron and of course below its solidification, that is when the metal exists as an aggregate of cementite and solid solution (saturated austenite) as explained in Chapter XXVI. It is not known whether the free or the dissolved cementite is graphitized first or whether the dissociation of both kinds proceeds simultaneously. Noting, however, that the graphitizing takes place more readily in the presence of a considerable quantity of combined carbon and, therefore, of free cementite, whereas in the presence of but little free cementite (cast iron with less than 2 per cent carbon) it is at best very slow and remains partial, it seems logical to infer that it is the free cementite which is first decomposed, indeed that its presence is necessary to cause the graphitizing of the dissolved cementite.

Annealing for "White Heart" Castings. — In the making of white heart castings a very large proportion of the carbon is removed by oxidation through the use (1) of an oxidizing packing, (2) of a high annealing temperature, and (3) of a long annealing. The original malleable castings made by Réaumur were of this type and his method

is still the prevailing one in Europe. The castings are annealed for four or five days at a temperature of 800 to 900 deg. C. By removing some castings from the annealing box from time to time and examining their structure the progress of the operation may be readily observed. The following transformations are noted as the operation progresses: (1) a narrow white rim of decarburized metal caused by the burning of the carbon from the outside of the casting and a dark center caused by the graphitizing of some of the cementite, (2) a broader white rim and a smaller and darker core due to the burning of more carbon and to the formation in the center of the casting of more graphitic carbon, the graphitizing of the cementite being now indeed possibly complete, (3) the fracture of the metal is now white and steely to the very center showing that most of the carbon has been removed by oxidation. These conclusions are fully confirmed by the microscopical examination of the structure of castings subjected to this annealing treatment for various lengths of time. As this oxidation of the carbon is necessarily a very slow process, white heart castings of small size only are made, generally not over $\frac{1}{2}$ inch thick. For malleablizing larger castings the "black heart" process soon to be described is decidedly superior.

White heart castings have a rather coarse fracture and structure because of the high and prolonged heating to which they were exposed. Since they resemble low carbon steels in composition and structure it would seem as if their properties could be very materially improved by suitable heat treatment as, for instance, by annealing followed by cooling in oil or in air according to their carbon content. Moldenke states that the European white heart malleable castings bend excellently and are very good, though slightly weaker than black castings.

Annealing for "Black Heart" Castings. — For the production of black heart castings, since the oxidation of carbon is of secondary importance, the annealing temperature need not be so high nor indeed is it necessary to use an oxidizing packing. As already mentioned, oxidizing packings are generally used, however, because of the apparent greater strength they impart to the castings. A certain amount of carbon, therefore, is burnt at the surface of the casting causing a narrow white rim while the core is very dark, hence the name of black heart given to these castings. This darkness of the core is due as we now understand it to the transformation of cement carbon into temper carbon.

The annealing temperature for the production of black heart castings is generally between 700 and 800 deg. C. in the case of air furnace iron, that is, but slightly above the critical range of the metal and the length of time at the full converting temperature between $2\frac{1}{2}$ and 3 days. Moldenke states that cupola iron castings should be annealed at temperatures some 65 to 120 deg. higher and writes:¹

"Just why there should be a difference in the temperature required for castings of the same composition when made in the cupola or in the air furnace, is one of the unsolved problems. It may be chemical in that the degree of oxidation has its effect on the opening up of the structure under the influence of heat. It may, on the other hand, be a matter of molecular physics, and depend on the constitution and structure of the castings as made, either in the contact of fuel with iron, or not. Possibly it may be a combination of both the chemical and the physical. Yet the problem still remains to be solved."

In completely malleablized black heart castings practically the whole of the car-

¹ A. Lissner writes that in cupola metal containing 0.25 per cent sulphur temper carbon begins to form at 760 deg. C.

bon should be present in the graphitic condition, the castings consisting then of a narrow case of decarburized iron and of a core made up of ferrite and particles of temper carbon, as shown in Figure 380. The structure of the core both before and after etching is further illustrated in Figures 381 and 382. If the malleablizing is but partial because of too low a temperature, too short a treatment, too little silicon, or for some other reason, considerable dissolved carbon may remain which in cooling through the critical range will give rise to the formation of pearlite. The structure of



Fig. 380. — Black heart malleable casting showing decarburized rim. Magnified 100 diameters. (Boylston.)

such partially malleablized cast iron is illustrated in Figure 383. It will be seen to consist of graphitic carbon, pearlite, and ferrite. The mechanism of the formation of such structures is obvious. At the end of the annealing treatment the metal consisted of a mass of austenite in which were embedded a number of particles of temper carbon; on slow cooling through the range the hypo-eutectoid austenite rejected some free ferrite until, its composition reaching the eutectoid carbon ratio, it was converted into pearlite. It will be noted that the pearlitic areas which should indicate the location of the residual austenite are situated away from the temper carbon particles, the latter being surrounded by ferrite.

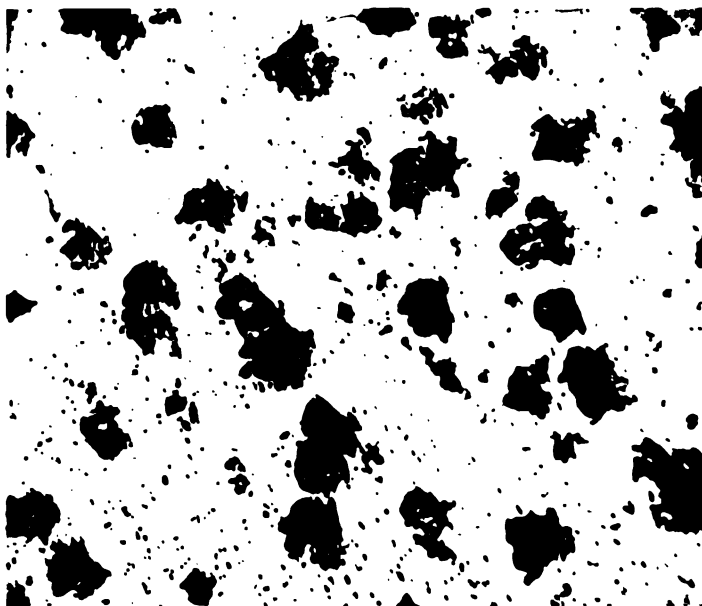


Fig. 381. — Black heart casting. Magnified 100 diameters. Not etched.
(F. C. Langenberg in the author's laboratory.)

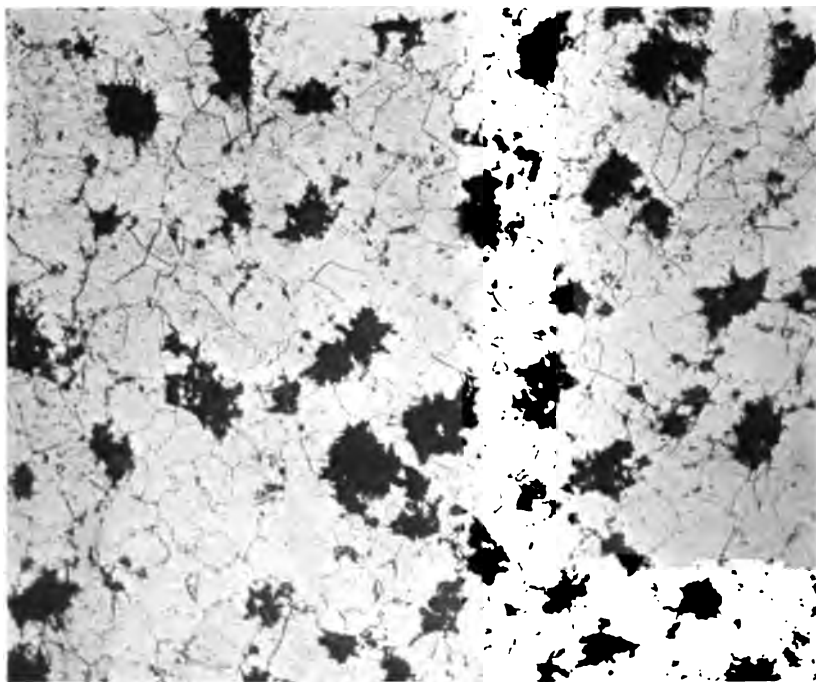


Fig. 382. — Black heart malleable casting. Magnified 100 diameters. Total carbon 2.64 per cent. Silicon 0.76 per cent. Phosphorus 0.137 per cent. Sulphur 0.031 per cent. Manganese 0.380 per cent. (Boylston.)

The annealing of white cast iron may be so incomplete as to retain so much dissolved carbon that in slow cooling free cementite as well as pearlite will be formed. In this case the austenite which existed above the range at the end of the annealing

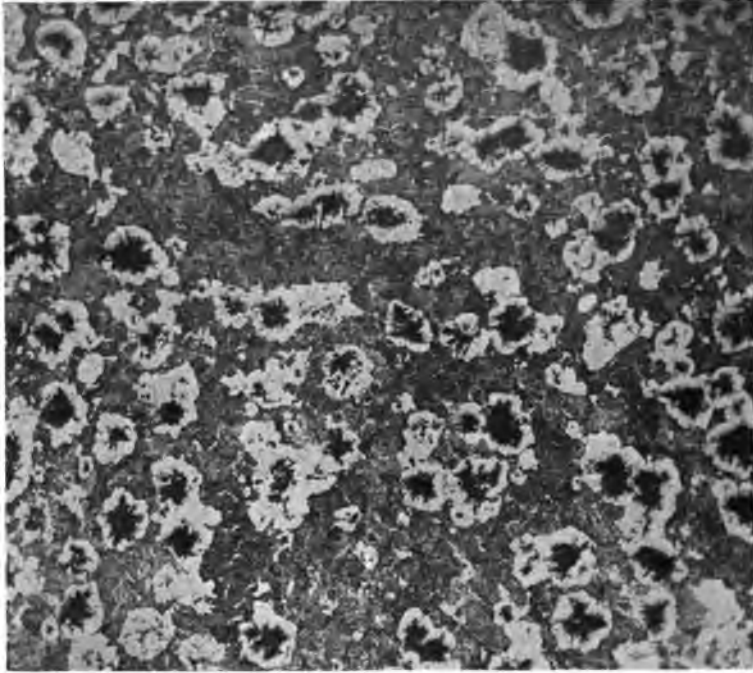


Fig. 383. — Partially malleablized cast iron. Magnified 100 diameters. Total carbon 2.55 per cent. Silicon 0.77 per cent. Phosphorus 0.164 per cent. (F. H. Franklin of Saunders and Franklin.)



Fig. 384. — Partially malleablized cast iron. Magnified 500 diameters. (Wüst.)

operation was hyper-eutectoid, that is, it contained more than 0.85 per cent, or thereabout, of dissolved carbon and on cooling through the range, therefore, liberated some free cementite. It is evident that partially malleablized cast iron, that is, cast

iron still containing considerable combined carbon, cannot be as malleable as malleablized cast iron free from combined carbon since its metallic matrix is necessarily less malleable.

Cooling from Annealing Temperature. — According to B. L. Leasman, the cooling from the annealing temperature to 1250 deg. F. should be very slow (42 hours) while below it may be rapid.

Gray Cast Iron vs. Malleable Cast Iron. — From the foregoing description of the nature and manufacture of malleable cast-iron castings it is evident that gray cast iron and malleable cast iron may have exactly the same chemical composition, although, of course, the former will generally contain more silicon and total carbon. In spite of identical or nearly identical composition, however, these two metals differ enormously in physical properties, gray cast iron being weak and brittle, malleable cast iron much stronger, and endowed with remarkable shock-resisting qualities. To account for this we must look into the microstructure of both metals when it will be observed that in gray cast iron the graphite occurs in large, generally curved, flakes and plates whereas in malleable cast iron it is present in small rounded particles, and it may well be conceived that the mode of occurrence of graphite in gray iron breaks up the continuity of the metallic matrix much more effectively, therefore, weakening it and destroying its ductility. Were it possible during the solidification of cast iron to cause the graphite to occur as it does in malleable cast iron, there is no reason to doubt but that it would be as strong and as ductile.

CHAPTER XXV

CONSTITUTION OF METALLIC ALLOYS

For many years vague and conflicting opinions were entertained in regard to the nature of metallic alloys. It was not known whether these intimate associations of two or more metals were merely mechanical mixtures or chemical compounds while the existence of solid solutions was unsuspected. The application to the study of metallic alloys of the determination of the solubility curves which had proved so fruitful in investigating the mechanism of the solidification of ordinary (liquid) solutions and of mixtures of melted salts, soon followed by the microscopical examination of their structure have at last revealed their true constitution. We know now that metallic alloys may be considered as solution of high freezing (solidification) point and, therefore, solid at ordinary temperature, whereas the old conception of solution applied only to substances liquid at that temperature. It is evident, however, that the location of the freezing-point of a substance in the temperature scale can have no bearing whatever upon its constitution, that is, upon the mode of occurrence of its constituents and the nature of the bond uniting them.

In these chapters the constitution of metallic alloys will be considered only so far as necessary to understand the equilibrium diagram described in Chapter XXVI in which steel and cast iron are considered as alloys of iron and carbon, i.e. as solutions of these elements, liquid at a very high temperature, frozen at ordinary temperature.

Since moreover steel and cast iron are considered as pure iron-carbon alloys it will suffice for our purpose to deal only with alloys of two metals, that is, with binary alloys.

The constitution of alloys is revealed chiefly (1) through the mechanism of their solidification as disclosed by their "fusibility" curves, and (2) through the microscopical examination of their structure after solidification.

Solidification of Pure Metals. — Let us first consider the solidification of a pure metal by observing its rate of cooling from the molten to the solid condition. This involves the use of a pyrometer, preferably a thermo-electric (Le Chatelier) instrument, the hot junction of which, suitably protected, is embedded in the cooling metal. By recording the successive intervals of time in seconds required for each successive cooling through ranges of temperature say of 10 deg. C., and plotting time against temperature a cooling curve of the type shown in Fig. 385 is obtained.¹ The teachings of such curves are obvious. Starting with the molten metal at *A*, its temperature being *T*, its cooling from *A* to *B*, while its temperature is falling from *T* to *T*_s is uniformly retarded. This results in the smooth, nearly straight portion *AB* of the curve. The cooling of a molten metal above its solidification point is in this respect similar to the cooling of any substance free from thermal critical points; the cooling curves

¹ Self-recording pyrometers may also be used.

obtained in such cases are always smooth curves indicating a uniform increase in time as the temperature of the substance falls. The curve of Figure 1 indicates the occurrence of a sharp critical point at the temperature T_s corresponding to the horizontal portion BC of the curve. It is evident that on reaching T_s the temperature of the metal suddenly ceased to fall and remained stationary during an interval of time represented by t' . The metal then resumed a normal rate of cooling which was continued to atmospheric temperature as indicated by the smooth portion CD which, were it not for the jog BC , would be a continuation of AB . We naturally connect this sudden appearance of a critical point in the cooling curve with the solidification of the

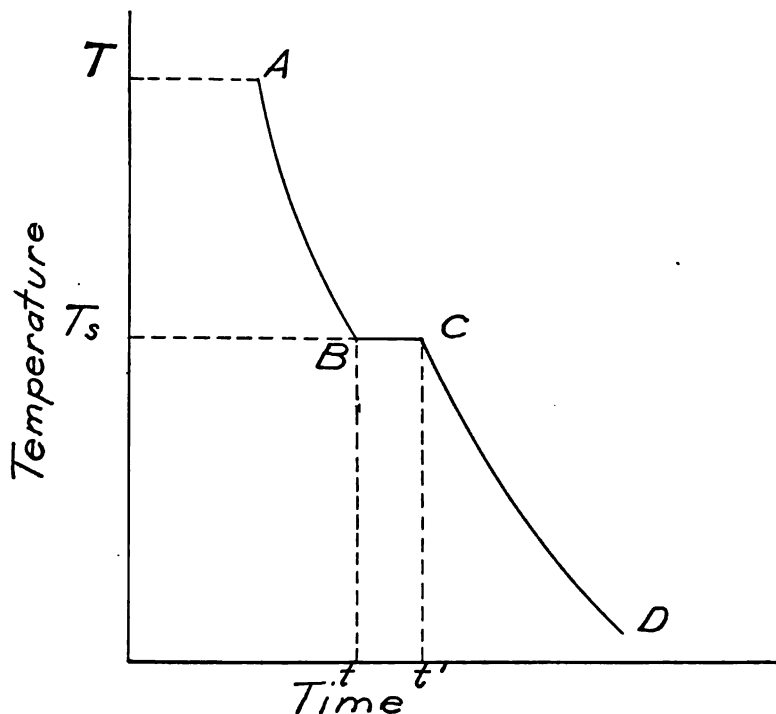


Fig. 385. — Typical cooling curve of pure metal.

metal. It clearly indicates (1) that the metal begins to solidify at the temperature T_s , (2) that while it is solidifying its temperature remains constant, (3) that the solidification lasts $t' - t$ seconds. It is evident that during its solidification the metal was exposed to the same cooling influences as those prevailing above and below it, and since its temperature nevertheless remains constant it must be that heat is here liberated in amount exactly sufficient to make up for the heat lost by radiation and conductivity. Any attempt at increasing the rate of cooling during solidification would result in hastening solidification and not in lowering the temperature of the metal. The heat evolved during the solidification of a substance is known as its "latent heat of solidification." In Fig. 385, AB then represents the cooling of the liquid metal, BC its solidification, and CD the cooling of the solidified metal. On heating a pure metal from below to above its melting-point, a similar curve is obtained indicating (1) that the melting-point coincides with the solidification point, at least under normal

conditions, and (2) that the melting takes place at a constant temperature, being, therefore, accompanied by an absorption of heat.

In Fig. 386 the cooling curves of several pure metals are shown. They differ only in regard to the location of the horizontal portions indicating the temperatures of solidification.

The structure of pure metals has been described in Chapter IV, when they were shown to be made up of polyhedral crystalline grains, each grain consisting of true crystals of uniform orientation. As an instance of the structure of pure metals, the structure of pure lead is shown in Figure 387.

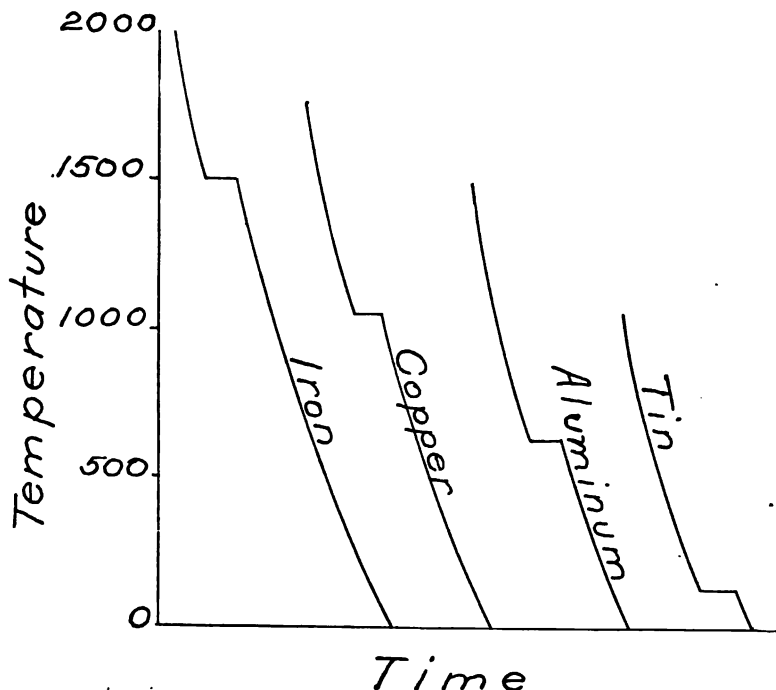


Fig. 386. — Cooling curves of various pure metals.

Solidification of Binary Alloys the Constituents of which Form Solid Solutions. —

The cooling or solidification curves of alloys of two or more metals may be constructed exactly like the cooling curve of a pure metal, namely, by observing the rate of cooling as the temperature is lowered from above the melting-point to atmospheric temperature and plotting the intervals of time against the corresponding temperature falls. A number of binary alloys are then found to yield cooling curves of the type shown in Fig. 388. From *A* to *B*, that is, as the alloy cools from *T* to *T_b*, the curve is smooth and, therefore, indicative of normal cooling. At *B* there is a sudden change of direction and from *B* to *C*, that is, from the temperature *T_b* to the temperature *T_c*, the cooling of the alloy is evidently abnormally slow. From *C* to *D*, that is, from the temperature *T_c* to atmospheric temperature, the cooling is again normal. Since the portion *BC* of the curve clearly indicates spontaneous evolutions of heat causing a marked retardation in the cooling of the alloy and lasting *t' - t* seconds, we naturally infer that it corresponds to its solidification. It follows from the appearance of the cooling curve

that alloys yielding such curves do not, like pure metals, solidify at a constant temperature but that their solidification, on the contrary, lasts $t' - t$ seconds while their temperature falls from T_b to T_c . Summing up, AB indicates the cooling of the molten alloy, B the beginning, and C the end of its solidification, t' the time required for its solidification, T_b T_c the fall of temperature during solidification, and CD the cooling of the solidified alloy. Above the point B , therefore, the alloy is entirely liquid, below C it is entirely solid, while between B and C it is partly liquid and partly solid. The point B is accordingly called the liquidus point and C the solidus point.

Binary alloys whose cooling curves are of the type shown in Fig. 388 are known to be solid solutions. In these alloys the component metals which are completely merged in the liquid condition remain likewise so completely merged after solidification that their separate existence cannot be detected by microscopical examination or



Fig. 387. — Pure lead. Magnified 20 diameters. (F. C. Langenberg in the author's laboratory.)

other physical means. They formed, on solidifying, homogeneous crystals containing both metals in indefinite proportions. These crystals are sometimes called "mixed crystals" and substances yielding them "isomorphous" mixtures by which it is meant that only isomorphous substances¹ can yield mixed crystals or in other words can form solid solutions. The expression "solid solution" is much preferable and is now quite universally used, at least by the English and French.

The mechanism of the formation of solid solutions of two metals should be examined more closely. Let us assume that a certain proportion of the metal M of relatively low melting-point is alloyed with, or dissolved in, the metal M' of higher melting-point. The metal M may be considered as the solute and M' as the solvent. It is believed that when solidification begins homogeneous crystals of M and M' are formed but that they contain a smaller proportion of the fusible metal M than the

¹ Isomorphous substances are those that are capable of crystallizing in the same crystallographic forms.

liquid bath, which is thereby enriched in M .¹ On further cooling these crystals grow but the crystalline matter now deposited contains more of the metal M than the crystals first formed, although still less than the molten bath which is further enriched in M and so on, the crystals growing through successive additions of crystalline matter containing increasing proportions of the dissolved and relatively fusible metal M , and approaching, therefore, although not reaching, the composition of the molten metal until finally the last drop solidifies. Meanwhile, as the temperature is lowered through and below the solidification range, diffusion takes place within the crystals so that finally they become chemically homogeneous provided time be given (through slow

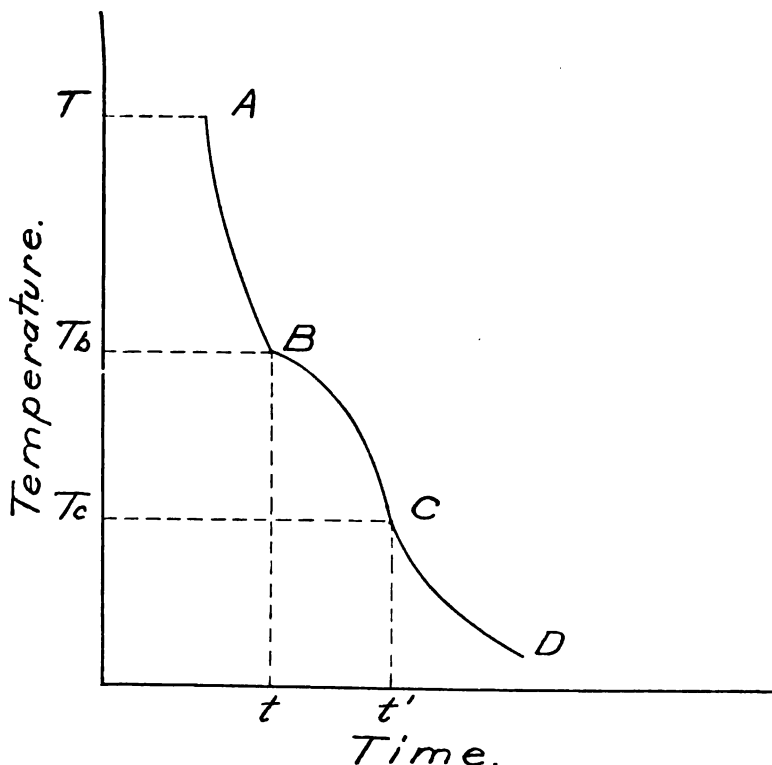


Fig. 388. — Typical cooling curve of binary alloy whose component metals form a solid solution.

cooling) for complete diffusion. Like pure metals, alloys whose component metals form solid solutions, are composed of polyhedral crystalline grains (see Fig. 389).

Fusibility Curves of Binary Alloys whose Component Metals are Completely Soluble in each Other when Solid. — So-called “fusibility curves” or “equilibrium diagrams” are obtained from any series of alloys by constructing the solidification curves, as explained above, of a number of alloys of that series and plotting on a single

¹ It is because the bath becomes richer in the more fusible metal M that its melting-point is lowered, resulting in its solidification covering a considerable and falling range of temperature. If the crystals first formed had the same composition as the bath, solidification would take place at a constant temperature. Witness the solidification of pure metals, of eutectic alloys, and of chemical compounds: the solidifying metal having the same composition as the liquid from which it forms, solidification takes place at a constant temperature.

diagram the evolutions of heat observed. This has been done in Fig. 390 by uniting the $BB'B'' \dots$ and the $CC'C'' \dots$ points denoting respectively the beginning and the end of the solidification of a number of alloys $AA'A'' \dots$. Leaving out the independent cooling curves used for the construction of the fusibility curve, the diagram shown in Fig. 391 is obtained, the co-ordinates being now temperature and composition. The figure is typical of the fusibility curves of binary alloys whose component metals are entirely soluble in each other when solid. They are composed of two branches, one concave the other convex, uniting the melting-points of the constituent metals. MLM' is known as the liquidus because any alloy of the series above that line is entirely liquid, while MSM' is called the solidus because any alloy below it is entirely solid. Within the area $MLM'SM$ the alloys are partly liquid and partly solid. The solidification of these alloys should be further described with the help of this diagram. Let us assume an alloy the composition of which is represented by the point P in the



Fig. 389. — Copper-zinc alloy. Copper 50 per cent. Magnified 200 diameters. Homogeneous solid solution. (Guillet.)

diagram and containing, therefore, 75 per cent of the low melting-point metal M and 25 per cent of the less fusible metal M' . An alloy of that composition at the temperature T is entirely liquid since its condition is represented by a point situated above the liquidus. As the alloy cools from P to l its temperature falling from T to t , it still remains entirely liquid. At l , temperature t , solidification begins through the formation of crystals whose composition must be represented by the point s at the intersection of the solidus and of a horizontal line through l , for it is evident that the only crystals that can be in equilibrium at the temperature t with the liquid of composition l must have the composition s . To clarify, if the crystals in equilibrium with the liquid l at the temperature t have not the composition s , then they must necessarily contain either more of the metal M' or less of that metal. In other words, their composition may be represented by the point x to the left of s or by the point y to its right. It is evident that the composition of the crystals forming at the temperature t from a liquid of composition l cannot have the composition x since the corresponding point falls within the area $MLM'SM$ and since any point in this area cannot represent the composition of the crystals existing at the corresponding temperature but must

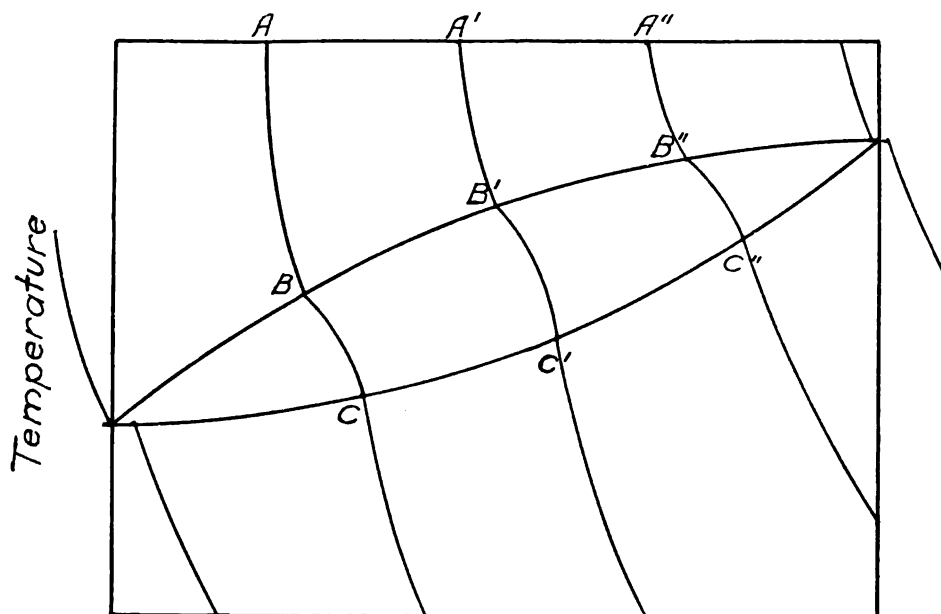


Fig. 390. — Diagram showing how fusibility curves are constructed.

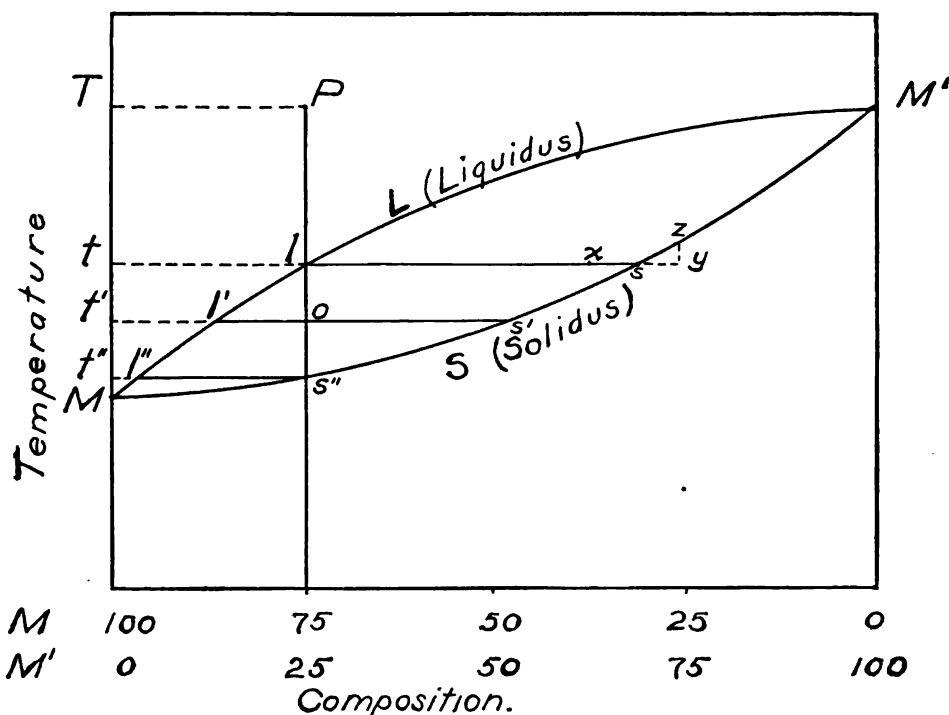


Fig. 391. — Typical fusibility curve of binary alloys whose component metals form solid solution.

represent on the contrary the *average* composition of the partly solidified alloy, hence the crystals forming at t in the case we are considering cannot have a composition represented by a point to the left of s . Assuming the composition of these crystals to

be represented by the point y to the right of s , then it is evident that these crystals must have formed at z , that is, at a temperature considerably higher than t , which cannot be since our alloy does not begin to solidify before the temperature t is reached. Hence the composition of the crystals forming at t , when the alloy P begins to solidify, cannot be represented by a point to the right of s . Clearly the point s must indicate the composition of those crystals. As the alloy cools from l to o , that is, from t to t' , the crystals which began to form at l continue to grow by gradual deposition of crystalline matter progressively richer in M while the remaining liquid bath likewise becomes richer in M and consequently more fusible, its varying composition being represented by u' . For any point o within the area $MLM'SM$, that is, when the alloy is in the process of solidification, the composition of the crystals in equilibrium at the corresponding temperature t' with the solution l' is represented by the point s' . This must

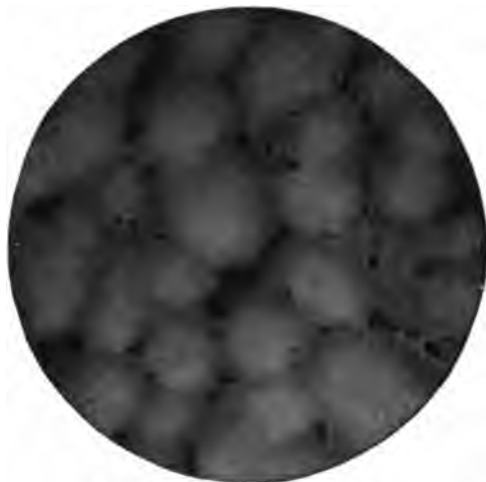


Fig. 392. — Iron-copper alloy. Copper 10 per cent. Magnified 125 diameters. Heterogeneous crystalline grains. The dark parts are richer in copper, the lighter parts richer in iron. (Stead.)

necessarily mean that as the metal cools from t to t' and while the crystals are growing, diffusion must necessarily take place in each crystal so that the concentric layers of varying composition of which we may conceive that they are initially composed, assume the same composition s' , the crystals being now homogenous. At s'' , temperature t'' , the solidification is complete. The last drop of liquid to solidify had the composition l'' . By diffusion the crystals, which began to form at s and grew from s to s'' , that is, as the temperature fell from t to t'' , have assumed a homogenous chemical composition. While this diffusion, however, needed to produce homogenous crystals, readily takes place during the crystallization of liquid solutions, the case is different with solid solutions. Unless solidification and subsequent cooling have been sufficiently slow, solid solutions may remain heterogenous, i.e. the different layers of crystalline matter of which each crystal is composed may not be of identical composition, the proportion of the most fusible metal increasing from center to outside (see Fig. 392). As an instance of binary alloys forming solid solutions the fusibility curve of gold-platinum alloys is reproduced in Figure 393.

Binary Alloys Forming Definite Compounds and Solid Solutions. — When two

metals unite to form solid solutions, it does not necessarily imply that they may not chemically combine with each other as well. Important instances are known of metals forming a definite chemical compound, which compound is then dissolved in the remaining excess metal. Two metals M and M' , for instance, may unite chemically to form the compound $MxM'y$ and unless the alloy contains the two metals exactly in the required atomic proportions, the compound may form a solid solution with the excess of metal M or of metal M' , as the case may be. In such cases the alloys should be considered not as alloys of two metals but of one metal and of one chemical compound of two metals, when the mechanism described to explain the solidification of solid solutions will be found applicable. Indeed we may conceive the existence of alloys of two metals in which two definite compounds are formed, mutually soluble and, therefore, forming solid solutions. Such alloys should be considered not as alloys

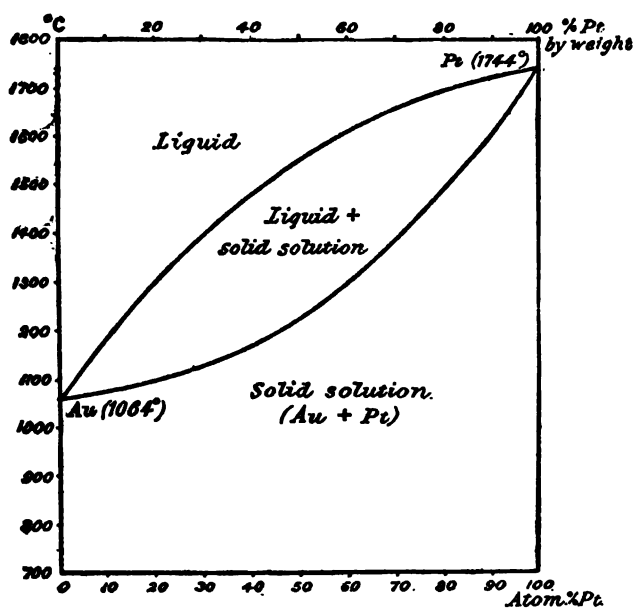


Fig. 393. — Fusibility curve alloys of gold and platinum. (Desch.)

of two pure metals but of two chemical compounds, the mechanism of their solidification being then identical to that of alloys of two metals.

Binary Alloys whose Component Metals are Insoluble in Each Other in the Solid State. — If two metals, although soluble in the liquid state, are insoluble when solid, it is evident that on solidification they must crystallize separately into distinct crystals readily distinguishable under the microscope, in other words, that the solid alloy must be an aggregate of the two metals. The study of the mechanism of the solidification of such alloys and of their microstructure should receive some attention.

The typical cooling or solidification curve of an alloy of two metals insoluble in each other when solid is shown in Figure 394. The curves are obtained as previously explained by observing the time required by the alloy to cool through successive and equal ranges of temperature and by plotting the times against the corresponding falls of temperature, or more conveniently and accurately by the use of self-registering pyrometers. The curve of Fig. 394 will be seen to consist of four parts, namely, AL

indicating a normal rate of cooling, LL' a retarded cooling, $L'S$ a stationary temperature, and SB a normal rate of cooling to atmospheric temperature. It is logical to infer that AL represents the uniform cooling of the liquid alloy and SB the uneventful cooling of the solid metal, L being the liquidus point, and S the solidus. The portion of the curve $LL'S$ represents the solidification of the alloy as the temperature falls from t to t' . It will be observed (1) that the solidification begins at L , temperature t , (2) that it proceeds from L to L' as the temperature is falling, and (3) that the end of the solidification takes place at a constant temperature, namely, t' , as indicated by the

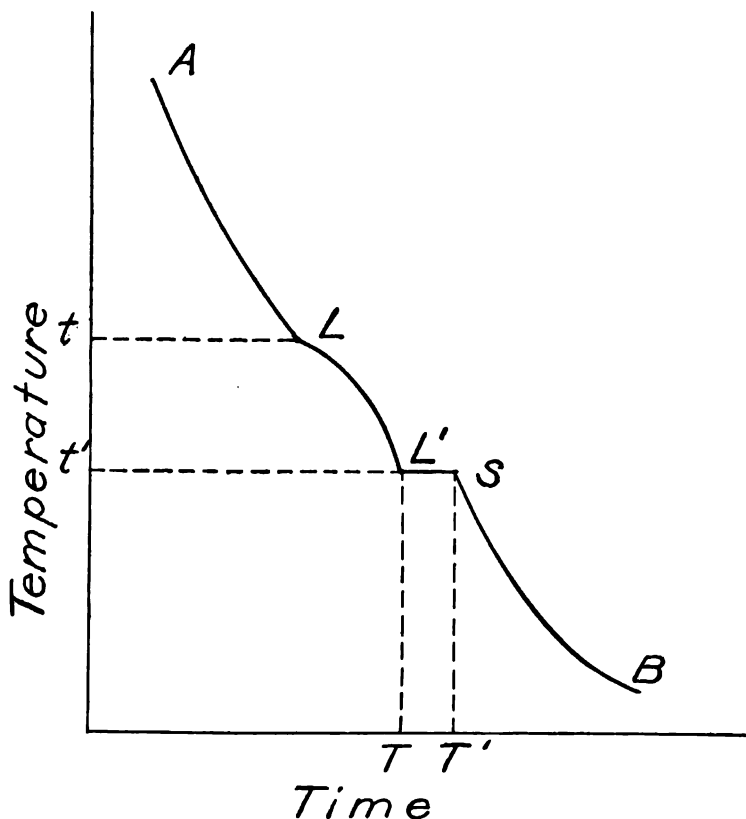


Fig. 394. — Typical cooling curve of binary alloy whose component metals are insoluble in each other in the solid state.

horizontal portion $L'S$, the temperature of the alloy remaining constant during $T' - T$ seconds.

In Fig. 395 the solidification curves of a number of alloys of the same series have been constructed as explained above, the alloys arbitrarily selected containing respectively 10, 20, 40, 60, and 80 per cent of metal M . It will be noted that, with the exception of the alloy containing 40 per cent of M , each alloy exhibits two evolutions of heat, namely an upper evolution, L , at varying temperatures and a lower, E , always at the same temperature regardless of the composition of the alloy. By uniting the upper points and the lower ones as indicated by dotted lines in Figure 395, the so-called fusibility curve or equilibrium diagram of that series of alloys is obtained. In Fig. 396 the fusibility curve only is represented, the independent cooling curves used for its

construction having been omitted. The co-ordinates are now composition and temperature. The curve indicates clearly the beginning and the end of the solidification

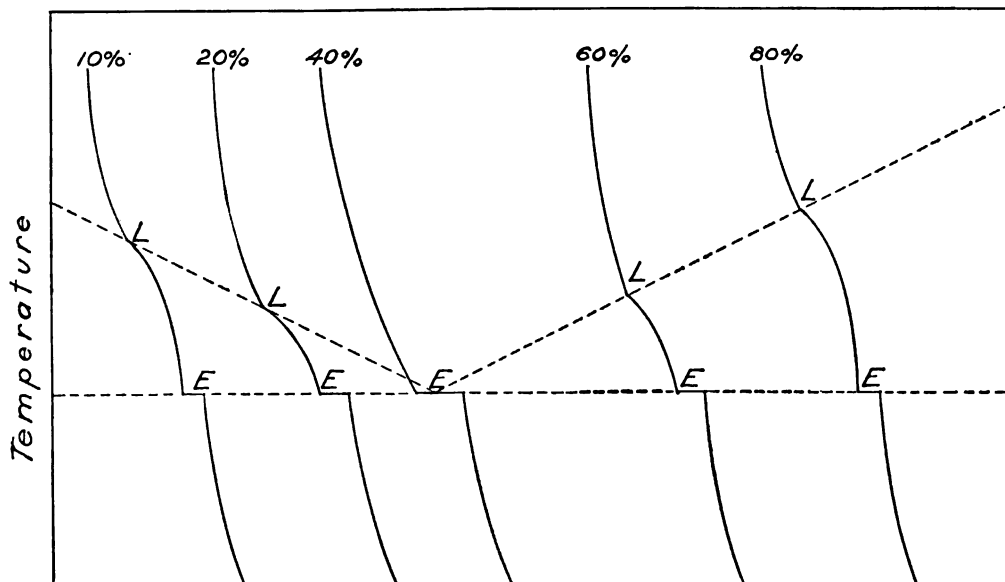


Fig. 395. — Diagram showing how fusibility curves are constructed.

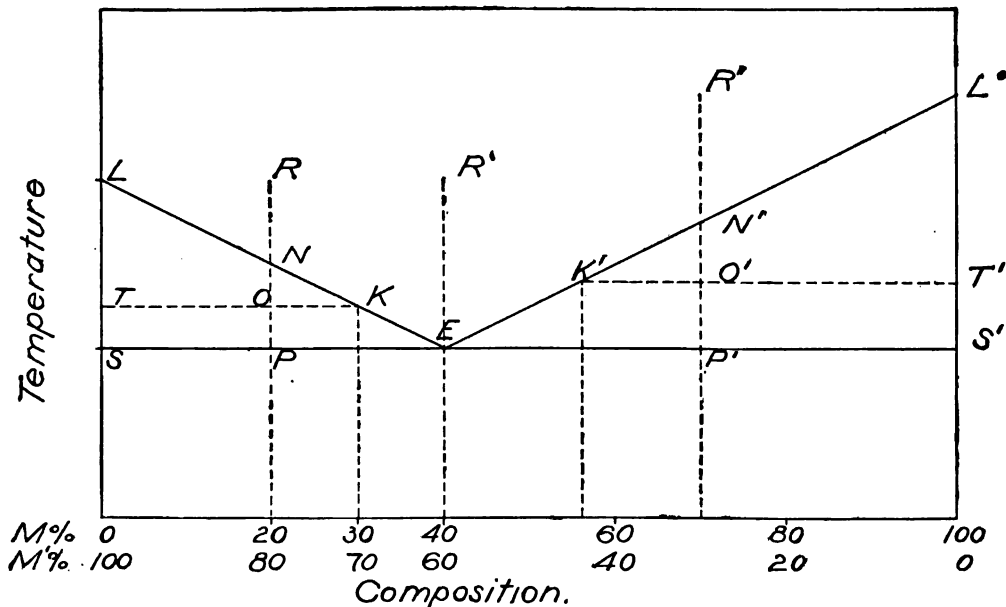


Fig. 396. — Typical fusibility curve of binary alloys whose component metals are insoluble in each other in the solid state.

of any alloy of the series. The solidification of an alloy whose composition corresponds to the point *R*, for instance, and which, therefore, contains 20 per cent of metal *M* and 80 per cent of metal *M'* evidently begins at *N* and ends at *P*. The fusibility curve is

made up of three branches, namely, the two intersecting lines LE and $L'E$ starting respectively from the melting-points of the two constituent metals and a horizontal line SS' passing by the point of intersection E of the first two. This is the typical fusibility curve of binary alloys whose component metals are insoluble in each other in the solid condition. The solidification of these alloys should now be examined more closely. Several features are obvious. The different alloys *begin* to solidify at different temperatures according to their composition. At first, as the percentage of M increases from 0 to 40 (a proportion arbitrarily selected), the solidification point is lowered from L to E , while with further increase of M from 40 to 100 per cent, the solidification point is raised from E to L' . The solidification of all alloys, however, *ends* at the same temperature, namely, at the temperature S . Clearly, LEL' is the liquidus and SES' the solidus. The alloy containing 40 per cent of M is evidently the most fusible alloy of the series since it remains liquid until the temperature S is reached while other alloys begin to solidify at higher temperatures. This alloy of lowest melting-point is known as the "eutectic" alloy, from the Greek meaning "well melting." It is evident that, like pure metals, eutectic alloys solidify at a constant temperature, namely the eutectic temperature. Many aqueous solutions also give rise to the formation of solutions of lowest freezing-points called "cryohydrates" and which were at first supposed to be true chemical compounds, that is, hydrates containing salt and water molecules in atomic proportions. And, likewise, eutectic alloys were at first supposed to be definite chemical compounds of the two metals. They are now known to be aggregates of these metals generally very finely divided. This will be made clear by following the solidifications of three alloys, R , R' , and R'' (Fig. 396). The alloy R contains, according to the diagram, 20 per cent of the metal M and 80 per cent of the metal M' . Since it contains less of the metal M than the eutectic alloy, we may for convenience refer to it as an hypo-eutectic alloy, although of course in regard to the content of M' it would be hyper-eutectic. In cooling from R to N the alloy remains liquid. At N solidification begins through the formation of pure crystals of M' , that is, of the metal which is present in excess above the eutectic ratio. The formation of pure crystals of M' continues as the alloy cools from N to P and meanwhile the portion of the alloy remaining liquid (we may call it the mother metal) becomes gradually richer in M , i.e. it approaches gradually the composition of the eutectic alloy. Finally at P , temperature S , the remaining liquid has exactly the eutectic composition and now solidifies at a constant temperature, the solidification temperature of the eutectic alloy. In other words, as the alloy cools from N to P with formation of pure crystals of metal M' the composition of the portion of the alloy remaining liquid varies according to the line NKE , reaching the composition E , that is, the eutectic composition, always at the same temperature regardless of the initial composition of the alloy. When the alloy has cooled to O , for instance, a point between LE and SE , it is partly liquid and partly solid, its temperature is T and the composition of the liquid portion is represented by K , that is, it contains 30 per cent of the metal M . On further cooling from O to P the composition of the mother metal shifts from K to E .

In the case of the alloy R'' , containing a larger proportion of the metal M than the eutectic alloy and which we may, therefore, consider to be hyper-eutectic, when it reaches the point N' its solidification begins, pure crystals of the metal M being formed while the molten bath becomes gradually richer in M' gradually approaching, therefore, the composition of the eutectic alloy, until at the temperature S that composition is reached when the remaining liquid solidifies at a constant temperature.

Any point O' situated between $L'E$ and $S'E$ indicates an alloy in part solid and in part liquid; its temperature is T' and the composition of the liquid is represented by K' . On cooling from O' to P' additional crystals of pure M are formed, or those already formed continue to grow while the composition of the molten metal shifts from K' to E .

Starting with the alloy R' of eutectic composition, it remains liquid until at E , temperature S , it solidifies at a constant temperature, there being no excess metal to be rejected.

Seeing that the branch LE corresponds to the formation of pure crystals of the metal M' and the branch $L'E$ to the formation of pure crystals of the metal M , the conclusion seems irresistible that their point of intersection E must correspond to the

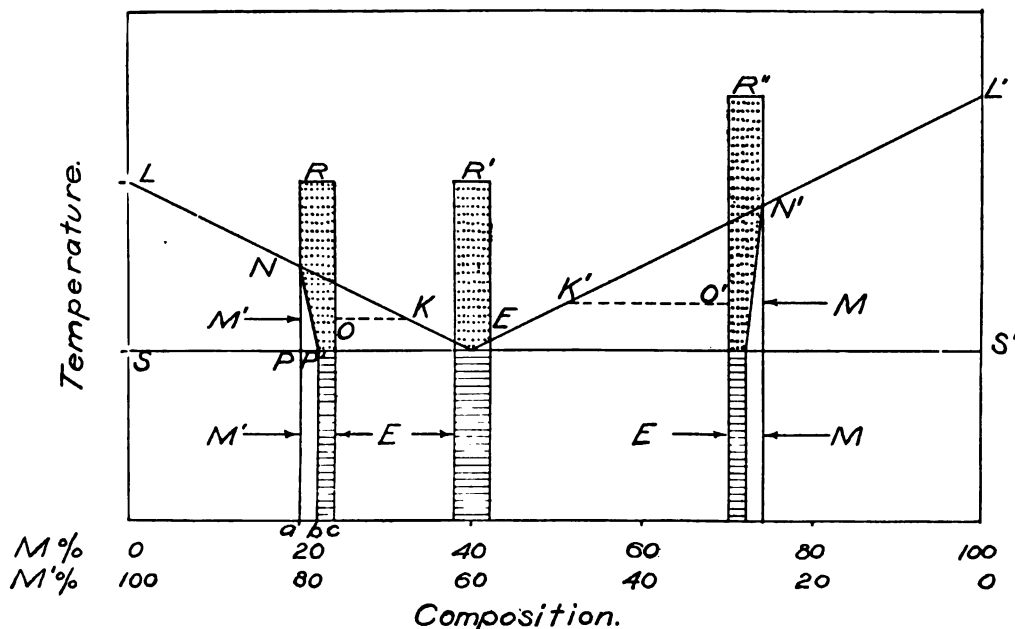


Fig. 397. — Diagram depicting the mechanism of the solidification of alloys whose component metals are insoluble in each other in the solid state.

simultaneous formation of crystals of metal M and of metal M' and that the eutectic alloy, therefore, must be a finely divided aggregate of M and M' . In other words, at any point on the branch LE , the alloy is saturated with the metal M' so that the lowering of its temperature must cause the separation of M' crystals with corresponding lowering of the saturation point, that is, of the solidification point of the bath. In a similar way, at any point on the branch $L'E$, the alloy is saturated with M and a fall in its temperature must result in the formation of M crystals while the solidification point of the portion remaining liquid is thereby lowered. At E the alloy is saturated with both metals so that any attempt at lowering its temperature must result in the simultaneous deposition of crystals of M and of M' , and since the composition of the bath remains the same, solidification now takes place at a constant temperature. Hence the constitution of eutectic alloys and the reason for their constant freezing temperature.

It has been attempted in Figure 397, to depict graphically the mechanism of the

solidification of hypo-eutectic, eutectic, and hyper-eutectic alloys. As diagrams of this kind have already been used in these lessons the present one will be readily understood.

When the alloy R , for instance, reaches the point N , crystals of M' form, their

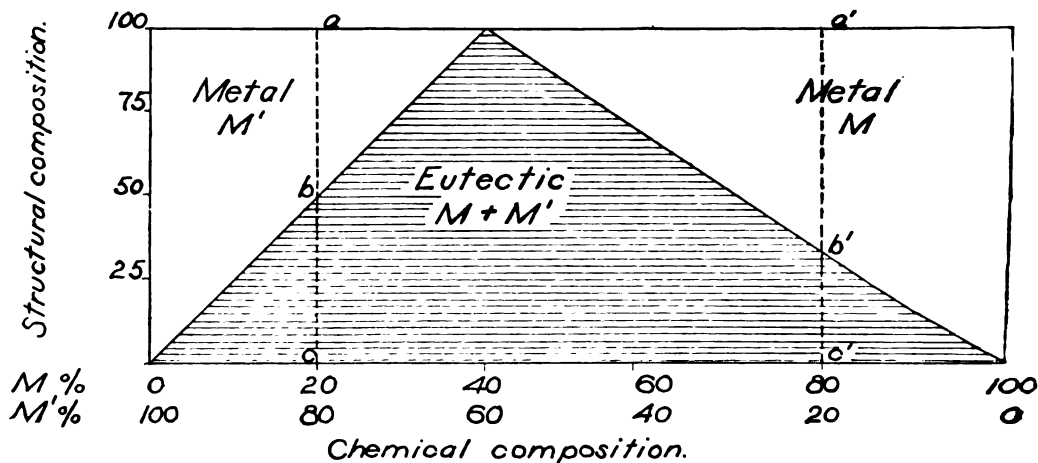


Fig. 398. — Diagram showing the structural composition of binary alloys whose component metals are insoluble in each other in the solid state.

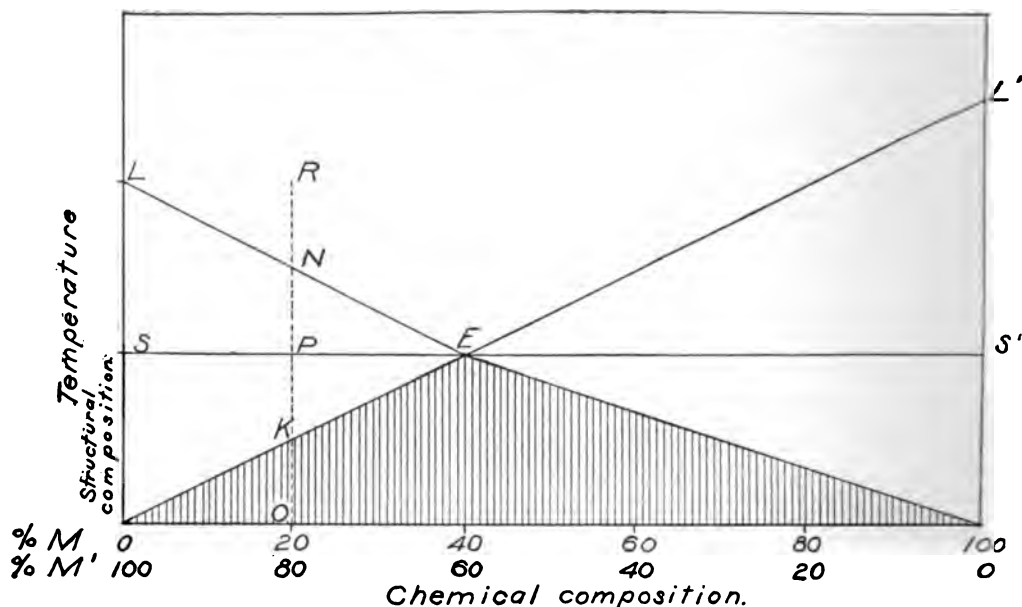


Fig. 399. — Diagram showing the fusibility curve and the structural composition of binary alloys whose component metals are insoluble in each other in the solid state.

formation as the metal cools from N to P being represented by the area NPP' . At P the residual liquid, now of eutectic composition, solidifies at a constant temperature. At any point O the composition of the portion still liquid is represented by K . The completely solidified metal will be made up of ab per cent of metal M and bc per cent of eutectic alloy.

It will not be necessary to describe at greater length the graphical representation of the solidification of the alloys R' and R'' .

The structural composition of alloys of two metals completely insoluble in each other in the solid condition may conveniently be represented graphically as shown in Figure

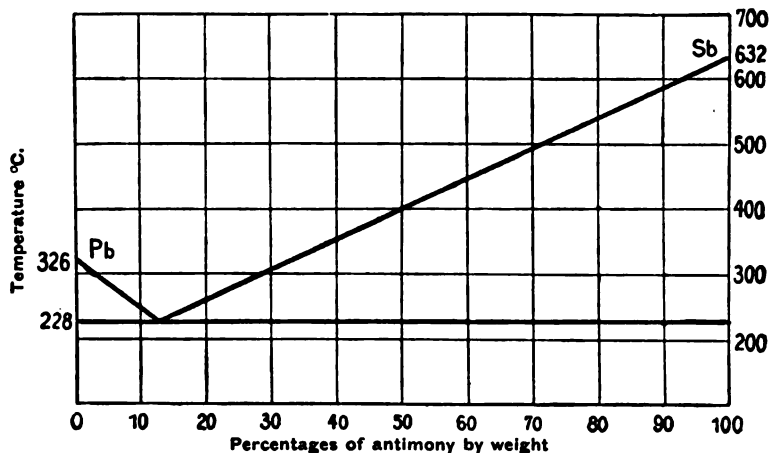


Fig. 400. — Fusibility curve of alloys of lead and antimony. (Roland-Gosselin.)



Fig. 401. — Typical structures of alloys whose component metals are insoluble in each other in the solid state. x , excess metal M' and eutectic; y , eutectic; z , excess metal M and eutectic. (Gulliver.)

398. The interpretation of this diagram is obvious. An alloy containing 20 per cent of the metal M , for instance, will be made up of ab per cent of M' and bc per cent of eutectic alloy. With 40 per cent of M the alloy is wholly of eutectic composition while with 80 per cent of M , for instance, it contains $a'b'$ of M crystals and $b'e'$ per cent of eutectic.

The composition diagram may with advantage be combined with the equilibrium diagram as it has been done in Figure 399. Taking an alloy whose composition is represented by *R*, for instance (20 per cent *M* and 80 per cent *M'*), it is seen (1) that it begins to solidify at *N*, (2) that as it cools from *N* to *P* pure crystals of *M'* are formed, (3) that the percentage of *M'* thus liberated is represented by *PK*, (4) that at *P* the remaining molten alloy now of eutectic composition solidifies, and (5) that *KO* represents the percentage of this eutectic alloy.

The graphical method used in these chapters for representing the structural composition of alloys was first suggested by the author in 1896. It has since been widely used and Tammann employs it to represent the heat liberated by the solidification of the eutectic or the time taken for its solidification, it being evident that both heat and time must necessarily be proportional to the *amount* of eutectic alloy formed. In

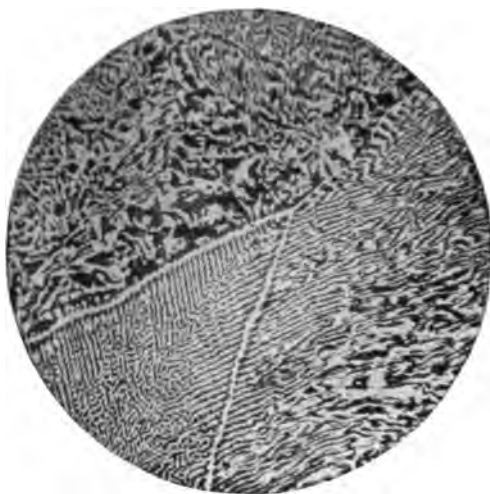


Fig. 402. — Eutectic alloy of bismuth and tin.
Magnified 200 diameters. (Desch.)

Fig. 399, therefore, the vertical distances of the shaded area are proportional to the times during which the temperature of the alloys remained constant while the residual baths of eutectic composition were solidifying. The fusibility curve of lead-antimony alloys is reproduced in Fig. 400 as an instance of alloys whose component metals are entirely insoluble in each other after solidification.

From the foregoing it appears that solidified alloys of two metals insoluble in each other are aggregates of these two metals and that three types of structure are to be expected (1) the structure of hypo-eutectic alloys composed of crystals or crystalline grains or particles of one metal embedded in, or surrounded by, some eutectic alloy, (2) the structure of hyper-eutectic alloys consisting of crystalline particles of the other metal and of eutectic alloy, and (3) the structure of eutectic alloys consisting of a finely divided aggregate of minute particles of both metals. These three types are represented diagrammatically in Fig. 401. Eutectic alloys are often made up of very thin alternate and parallel plates or lamellæ of each of the two constituents, but in some cases they consist of rounded or elongated particles of one of the constituents embedded in a matrix of the other constituents. The structures of some

eutectic alloys are shown in Figures 402 to 404. It will be noted that the constituents of eutectic alloys are not always pure metals.

Binary Alloys whose Component Metals are Partially Soluble in each Other when Solid. — Metals are seldom absolutely insoluble in each other when solid, each metal

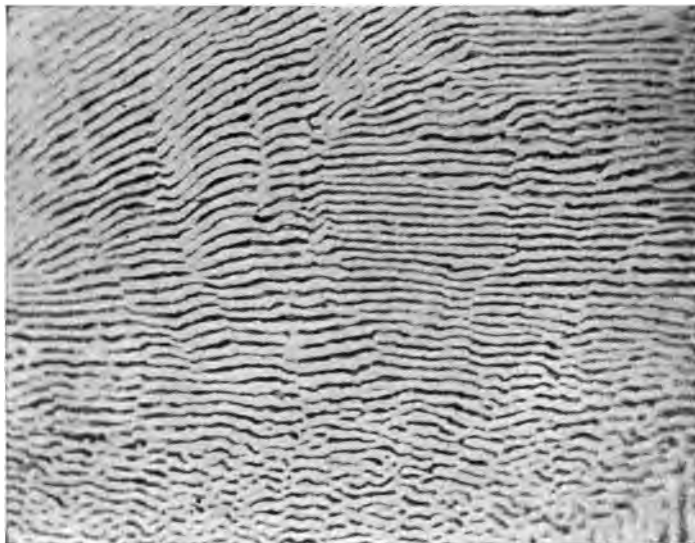


Fig. 403. — Eutectic (eutectoid) alloy of iron and Fe_3C . Pearlite. Magnified 1000 diameters. (Law.)

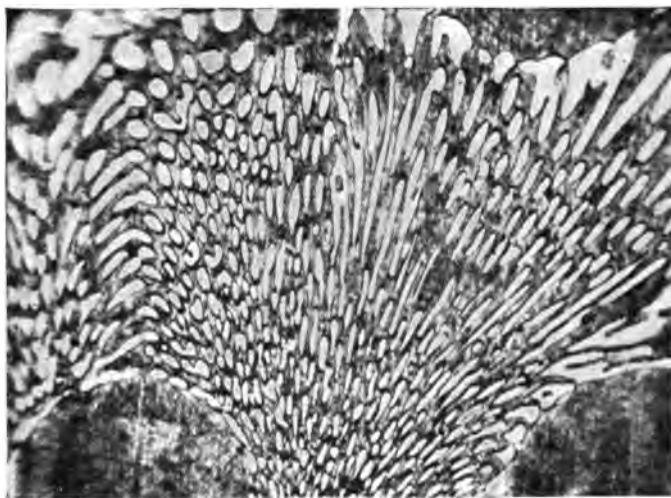


Fig. 404. — Eutectic alloy of SnCu_4 and Cu_3P . Magnified 1000 diameters. (Law.)

in the majority of cases being capable of retaining in solid solution a small percentage of the other metal. The modifications which such partial solubility introduces in the fusibility curve should be considered. Let us suppose two metals M and M' and let us assume that the metal M' is capable of retaining in solution immediately after

solidification, i.e. at the eutectic temperature, 5 per cent of the metal M and that the metal M can retain in solid solution 10 per cent of the metal M' . The fusibility curve of these alloys constructed in the usual way will have the appearance indicated in

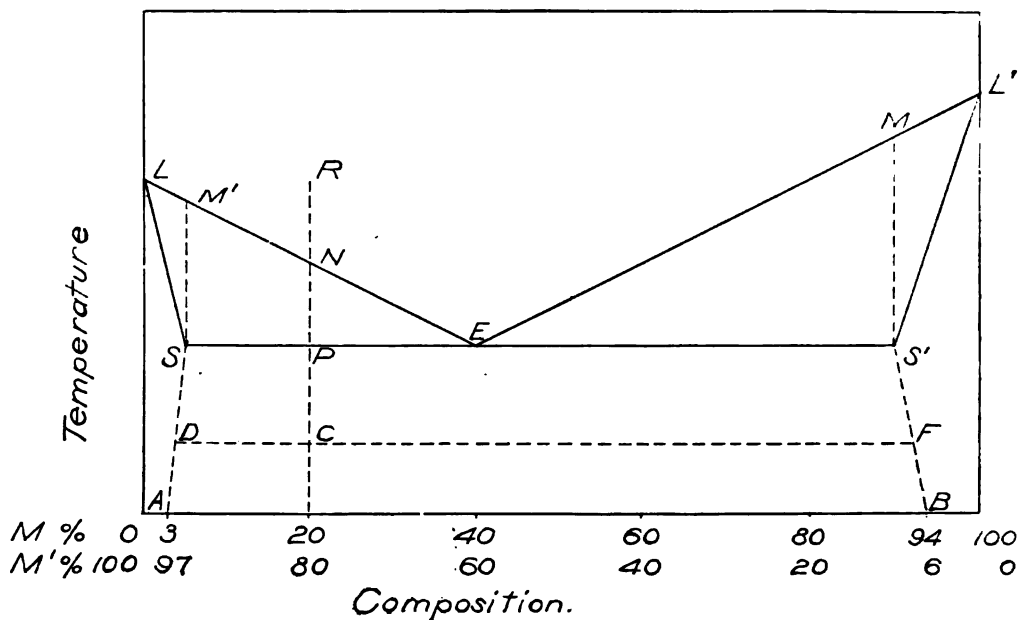


Fig. 405. — Typical fusibility curve of alloys whose component metals are partially soluble in each other in the solid state.

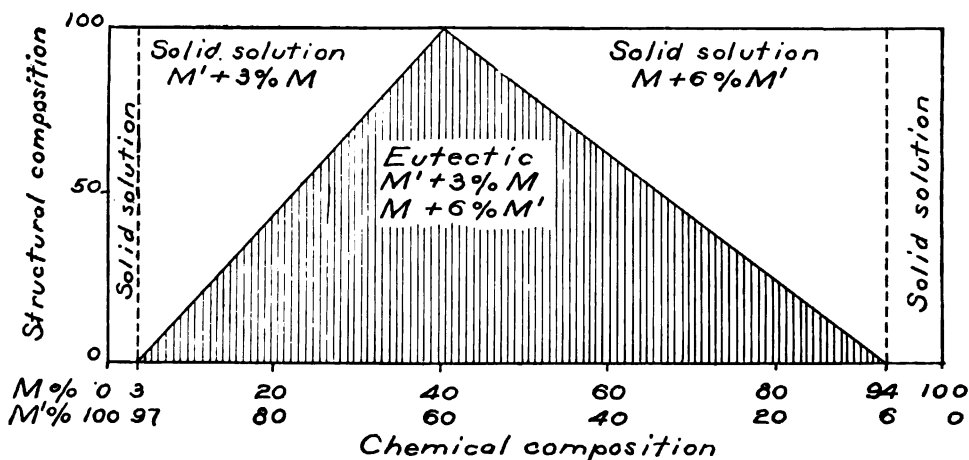


Fig. 406. — Diagram showing the structural composition of binary alloys whose component metals are partially soluble in each other in the solid state.

Figure 405. By comparing it with the fusibility curve of metals entirely insoluble (Fig. 396) it will be noted that the only differences between them are (1) that the eutectic line SES' instead of extending over the whole length of the diagram now stops at the points S and S' corresponding respectively to 5 per cent of metal M and to 10

per cent of metal M' , and (2) the introduction of the branches SA and $S'B$ indicates the changes of solubility of the metals as the alloys cool from the eutectic to atmospheric temperature. These curves show that at atmospheric temperature M' retains in solution 3 per cent of M and that M retains in solution 6 per cent of M' . LEL' is the liquidus, $LSES'L'$ the solidus. Clearly, any alloy containing less than 5 per cent of the metal M or less than 10 per cent of the metal M' solidifies as a solid solution, the diagram showing the absence of eutectic alloys. In other words, alloys containing from 0 to 5 per cent of M may be considered as alloys of M' and of a solid solution of M' plus 5 per cent of M , LM' being the liquidus and LS the solidus of such alloys and their solidification taking place as explained in the case of any two metals forming solid solutions. And, likewise, alloys with less than 10 per cent of M' may be regarded as alloys of the metal M and of a solid solution of M plus 10 per cent of M' , their liquidus being represented by $L'M$ and their solidus by $L'S'$. For all alloys containing between 5 and 90 per cent of M the diagram shows that a eutectic alloy is formed and that the mechanism of the solidification is apparently the same as the one

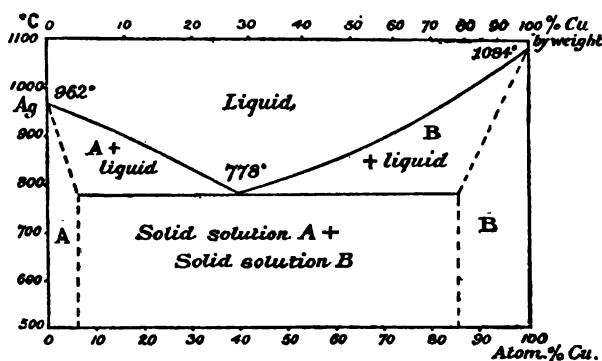


Fig. 407. — Fusibility curve of alloys of silver and copper.
(Desch.)

described in the case of alloys of insoluble metals. It should be noted, however, that the two components of these alloys are no longer the pure metals but two solid solutions, namely, a solution of M' containing 5 per cent of M and a solution of M containing 10 per cent of M' , one of these solid solutions, therefore, crystallizing when the temperature of the alloy reaches any point on the lines LEL' and the eutectic alloy being made up of a fine conglomerate of these two solid solutions. To clarify let us consider an alloy represented by the point R , Figure 405. At N its solidification begins, crystals of a solid solution of M' containing 5 per cent of M being formed. At P the residual molten mass, having reached the eutectic ratio, crystallizes at a constant temperature as a fine aggregate of the two solid solutions. Since the mutual solubilities of the metals M and M' decrease, however, as the alloy cools below the eutectic temperature, it is evident that each crystal must undergo a gradual transformation. These transformations are indicated by the branches SA and $S'B$. After the solidification of the eutectic, all alloys are aggregates of the two solid solutions whose compositions are represented by the points S and S' , that is, in the case under consideration, arbitrarily, M' plus 5 per cent of M and M plus 10 per cent of M' . At atmospheric temperature all alloys are aggregates of two solid solutions whose compositions correspond to the points A and B , that is in the case considered M' plus 3 per cent of M

and M plus 6 per cent of M' . At any point below the eutectic line, the corresponding alloy is an aggregate of two solid solutions whose compositions are indicated by the corresponding points on the branches SA and $S'B$. At C , for instance, in case of alloy R , the structure is composed of free crystals of solid solution D and of eutectic, the com-



Fig. 408. — Silver-copper alloy. Copper 15 per cent. Magnified 600 diameters. Dark constituent is silver containing a little copper. (Osmond.)



Fig. 409. — Silver-copper alloy eutectic. Copper 28 per cent. Magnified 600 diameters. (Osmond.)

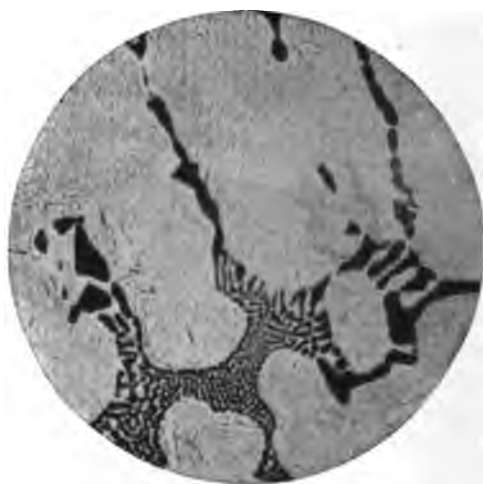


Fig. 410. — Silver-copper alloy. Copper 65 per cent. Magnified 600 diameters. Light constituent is copper containing a little silver. (Osmond.)

ponents of which are solid solution D and solid solution F . In other words, as the alloy cools from the eutectic line to atmospheric temperature, the composition of its two constituents shifts respectively from S to A and from S' to B .

The structural composition of alloys whose component metals are partially soluble when solid may be represented in the usual way as shown in Figure 406. Its interpre-

tation does not call for further elaboration. Between 0 and 3 per cent of M and between 0 and 6 per cent of M' , solid solutions are formed of corresponding compositions. Between 3 and 40 per cent of M , the free solid solution formed is saturated with M , and between 40 and 94 per cent of M it is saturated with M' , while the eutectic is made up of the two saturated solutions. The fusibility curve of silver-copper alloys is shown in Figure 407 as an example of alloys whose components remain partly soluble in each other after solidification and typical structures of these alloys are given in Figures 408 to 410.

CHAPTER XXVI

EQUILIBRIUM DIAGRAM OF IRON-CARBON ALLOYS

Fusibility Curve of Iron-Carbon Alloys. — Steel and cast iron are essentially alloys of iron and carbon, and their fusibility curve or equilibrium diagram may be constructed as in the case of any binary alloy, namely, by determining the independent cooling curves of a number of alloys of the series and plotting the evolutions of heat

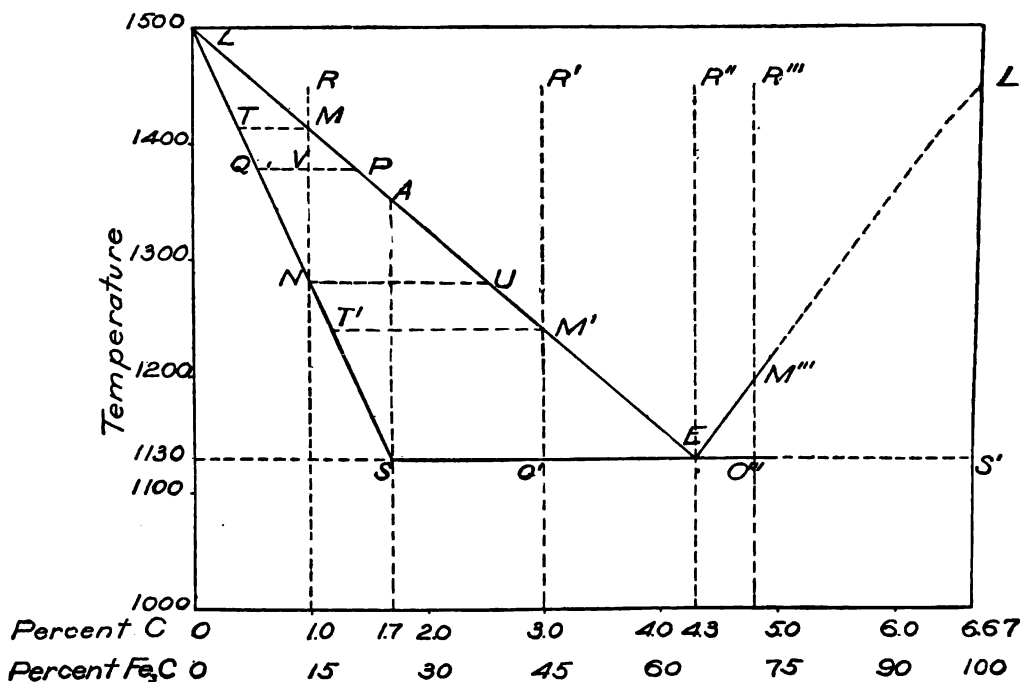


Fig. 411. — Fusibility curve of iron-carbon alloys.

noted against the corresponding temperatures. The resulting curve is shown in the diagram of Figure 411.

While it is not generally possible for molten iron slightly above its melting-point to dissolve more than 5 per cent of carbon, the diagram has been constructed so as to include a percentage of carbon up to 6.67 per cent which corresponds to 100 per cent Fe₃C. That portion of it, however, corresponding to more than 5 per cent of carbon, has been drawn in dotted lines. The complete equilibrium diagram should include the evolutions of heat occurring after solidification, known as the critical points, which have been fully described in these chapters, but they are purposely left out of the diagram of Fig. 412, it being desired first to confine our attention to the mechanism

of the *solidification* of iron-carbon alloys. In view of the explanation of the meaning of fusibility curves given in Chapter XXV, it will be evident that iron and carbon alloys are partially soluble in each other when solid, that LEL' is their liquidus and LSS' their solidus and that the point E indicates the formation of a eutectic alloy. As carbon increases from 0 to about 1.70 per cent, the alloys solidify as solid solutions of corresponding carbon content, LA being the liquidus and LS the solidus. These solid solutions considered as microscopical constituents are called austenite. The solidification of alloys containing between 1.7 and 4.3 per cent carbon begins when their temperature reaches the line LE , crystals of a solid solution finally containing 1.70 per cent carbon (then called saturated austenite), being formed which keep on growing until the line SS' , temperature 1130 deg., is reached when, clearly, a eutectic

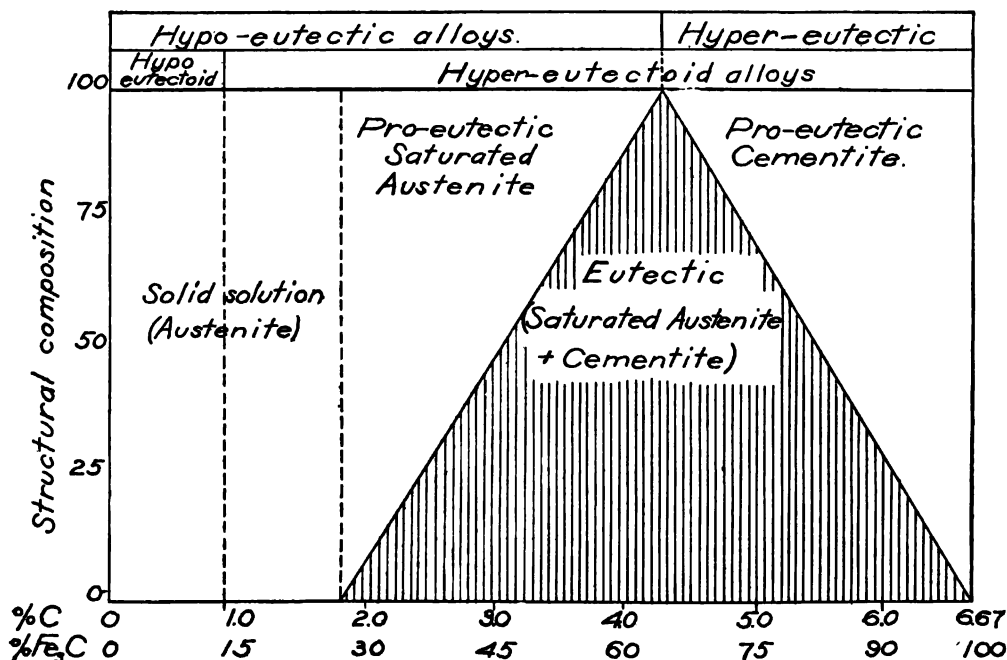


Fig. 412. — Structural composition of iron-carbon alloys immediately after their solidification.

is formed composed of that solid solution and of another constituent. The nature of the other constituent present in the eutectic alloy formed during the solidification of iron-carbon alloys has been in dispute. It seems at first natural to infer that elemental carbon, i.e. graphite, is that constituent, in which case the eutectic alloy would be made up of minute crystalline particles alternately of saturated austenite and of graphite. Many evidences, however, point to carbon being dissolved in molten iron as the carbide Fe_3C (cementite) and to its always solidifying as Fe_3C , although, as later explained, it may break up into iron and graphite ($Fe_3C = 3Fe + C$) immediately after its solidification. If this hypothesis be correct, it follows that the eutectic alloy must be a mechanical mixture of minute particles of saturated austenite and of Fe_3C . It would seem at first as if the microscopical examination of alloys of suitable compositions should readily reveal the nature of the eutectic alloy. It will soon be seen, however, that both cementite and graphite are generally found in solidified eutectiferous alloys, the microscopical test leaving us in doubt as to which of the two constitu-

ents formed first. In the author's opinion it seems more probable that when an iron-carbon alloy containing more than some 1.7 per cent carbon solidifies, a eutectic of saturated austenite and of cementite is always produced, or in other words, that in the diagram of Figure 411 the curve $L'E$ indicates the crystallization of cementite and not of graphite. The opposite view will be considered later. Let us now follow the solidification of four typical alloys, namely, R , R' , R'' , R''' , containing respectively 1 per cent, 3 per cent, 4.3 per cent, and 4.8 per cent of carbon, the first two being, therefore, hypo-eutectic alloys, the third the eutectic alloy, and the fourth a hyper-eutectic alloy. As the alloy R cools, it begins to solidify at M through the formation of crystals of a solid solution the composition of which is represented by the point T on the solidus. On cooling from M to N these crystals grow through successive additions of crystalline matter, the composition of which varies from T to N while the composition of the molten bath shifts from M to U , the last drop solidifying having the composition U . As soon as the crystalline matter is deposited, however, at least if time be given, diffusion takes place through each crystal so that finally they are chemically homogeneous and of composition N , the completely solidified metal being composed of homogeneous crystalline grains of austenite containing one per cent carbon.

At any temperature V between the solidus and the liquidus the crystals in equilibrium with the molten metal must have the composition Q . It may at least be conceived that if the cooling through and below the solidification period be rapid, the crystalline grains of austenite will not be chemically homogeneous, complete diffusion having been prevented.

In the case of an alloy whose composition is represented by the point R' in the diagram, it begins to solidify at M' (some 1230 degrees C.), when crystals of iron containing carbon in increasing proportions up to 1.7 per cent begin to form, the composition of the molten metal meanwhile shifting from M' to E . At O' , temperature 1130, the residual molten mass has reached the eutectic composition and now solidifies at a constant temperature, namely, the eutectic temperature, the completely solid metal being made up of crystalline grains of saturated austenite surrounded by a eutectic alloy composed of minute crystals of saturated austenite and minute crystals of cementite.

The alloy R'' has the eutectic composition (4.3 per cent carbon). It remains liquid until its temperature falls to 1130 deg. C. when it solidifies at a constant temperature after the fashion of eutectic alloys.

The alloy R''' contains more carbon than the eutectic alloy. On reaching its solidification point M''' crystals of cementite begin to form, increasing in size as the metal cools from M''' to O''' while the composition of the bath shifts from M''' to E . At O''' the residual molten mass having now the composition of the eutectic alloy, freezes at a constant temperature, the completely solidified alloy being made up of crystals of cementite embedded in a ground mass consisting of the eutectic alloy.

Structural Composition of Iron-Carbon Alloys Immediately after Solidification. — The structural composition of iron-carbon alloys *immediately after their solidification*, assuming that Fe_3C and not graphite forms, may be represented in the usual way by the diagram of Figure 412. The diagram clearly shows (1) that alloys containing less than 1.70 per cent of carbon are made up wholly of solid solutions, (2) that alloys containing between 1.70 and 4.3 per cent carbon are made up of decreasing proportions of saturated austenite and increasing proportions of eutectic, (3) that alloys containing exactly 4.3 per cent of carbon are composed entirely of eutectic, and (4) that alloys containing more than 4.3 per cent carbon contain an increasing amount of free

cementite, and decreasing amount of eutectic the latter disappearing altogether when the metal contains 6.67 per cent carbon.¹

A modified form of the structural composition diagram may profitably be combined

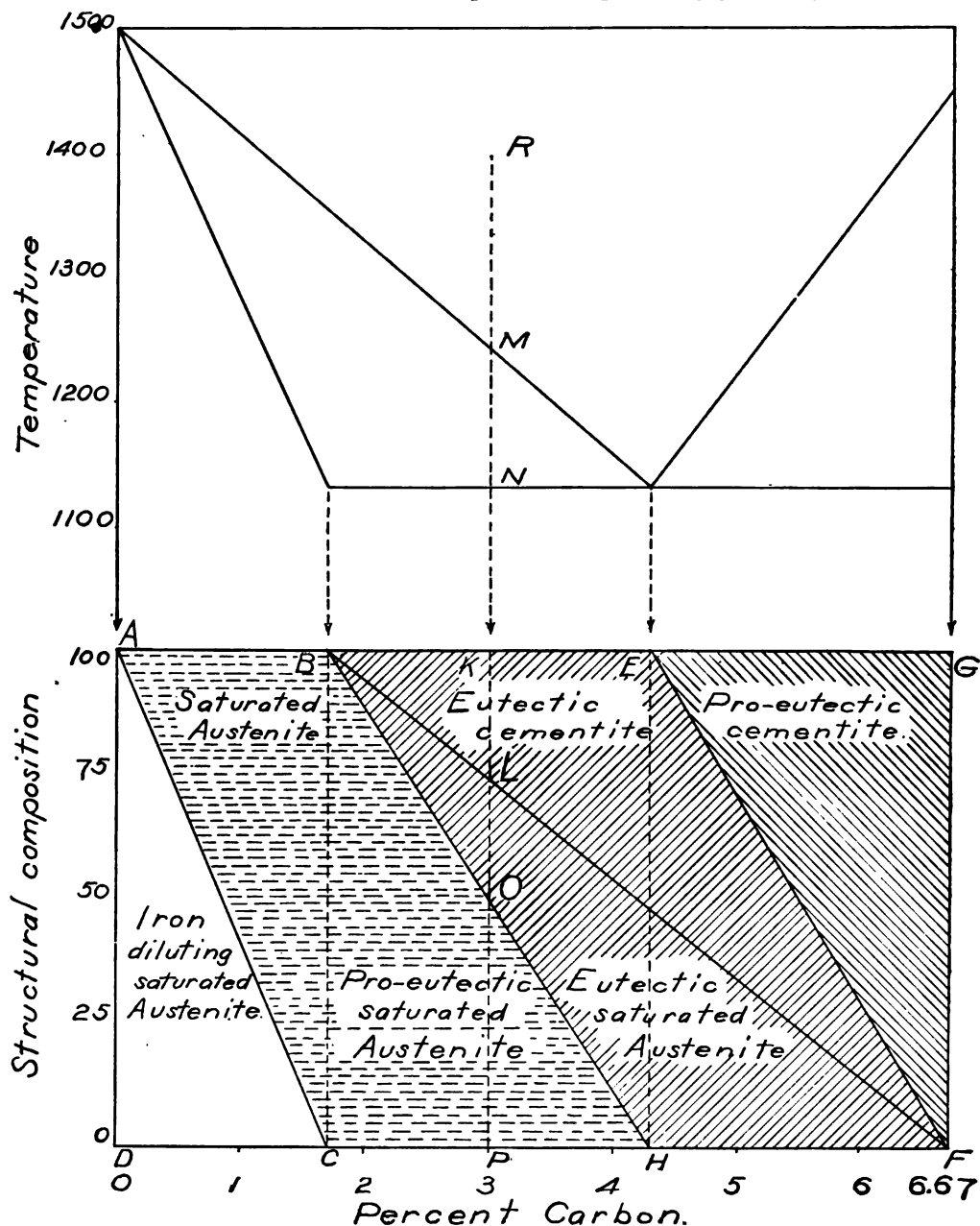


Fig. 413. — Fusibility curve and structural composition diagram of iron-carbon alloys.

with the equilibrium diagram as shown in Figure 413. Its interpretation should be obvious. The area *ABCD* represents the structural composition of all alloys containing less than 1.7 per cent of carbon, and shows that they are made up of 100 per cent

¹ Howe questions the existence below solidification of pro-eutectic cementite on the ground that it graphitizes as soon as formed unless the cooling be extremely rapid or considerable manganese present.

of austenite. By dividing this area by the line AC , however, it is further shown graphically that the composition of the austenite of these alloys varies, and that they may be considered as being made up of ABC saturated austenite *diluted* by ADC pure iron, clearly indicating that with 0 carbon the alloy is entirely made up of iron and with 1.7 per cent carbon entirely of saturated austenite. The area BCH represents the proportion of free (pro-eutectic) saturated austenite formed during the solidification of any alloy containing between 1.70 and 4.3 per cent carbon. The area $BEFH$ represents the proportion of eutectic present in any alloy containing more than 1.7 per cent of carbon. By dividing this area in two portions, moreover, by means of the line BF we show graphically the relative proportions of saturated austenite and of cementite in the eutectic. Finally, the area EGF indicates the percentage of pro-eutectic

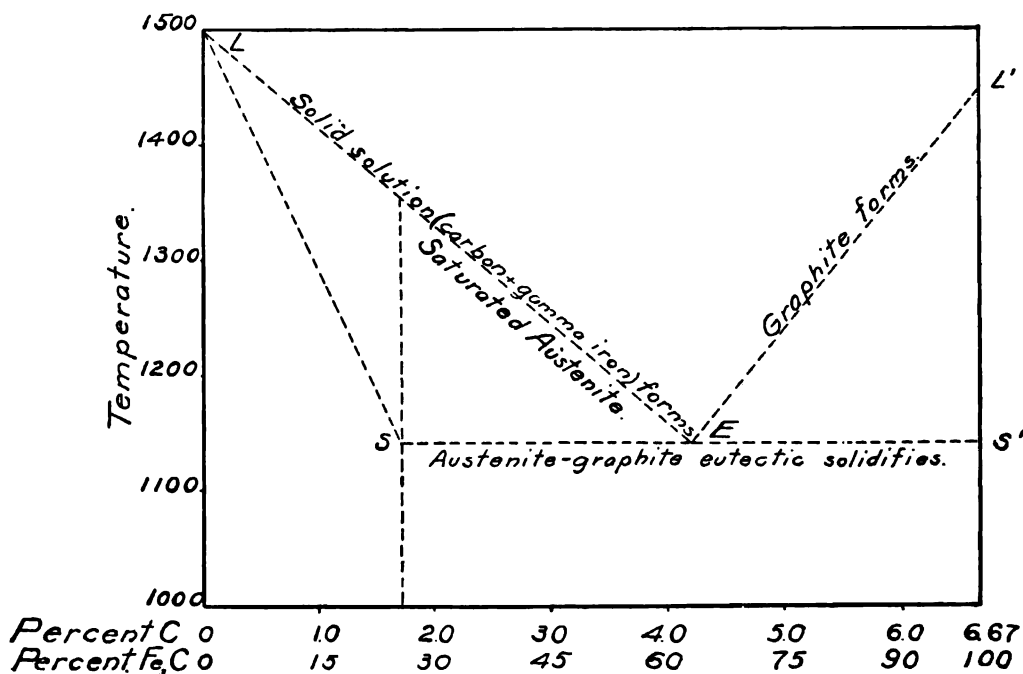


Fig. 414. — Iron-graphite fusibility curve of iron-carbon alloys.

cementite in any alloy containing more than 4.3 per cent carbon. To clarify, let us consider the alloy of composition R (3 per cent carbon). As it cools from M to N an amount of saturated austenite crystallizes, represented in percentage by the line OP of the structural composition diagram. At N an amount of eutectic alloy is formed, represented by the distance KO made up of KL per cent of cementite and LO per cent of saturated austenite.

The percentage of cementite and of saturated austenite in the eutectic may be readily calculated by solving the equations

$$(1) A + C_m = 100$$

$$(2) \frac{1.7}{100} A + \frac{6.67}{100} C_m = 4.30$$

in which A represents the percentage of austenite, and C_m the percentage of cementite in the eutectic alloy and which express the facts that the carbon present in the eutectic

(4.3 per cent) is divided between the austenite and the cementite, the former containing 1.7 per cent carbon, the latter 6.67 per cent. The resolution of these equations shows that the eutectic alloy contains nearly 47.7 per cent of saturated austenite and 52.3 per cent of cementite. The structural composition of any iron-carbon alloy *immediately* after its solidification may likewise be readily calculated. If it contains less than 1.70 per cent carbon it is entirely made up of austenite. If more highly carburized, two cases are to be considered: (1) the alloy contains between 1.7 and 4.3 per cent carbon when it is made up of saturated austenite (A) and of eutectic (E) and (2) the alloy contains between 4.3 per cent and 6.67 per cent carbon when it is composed of cementite (Cm) and of eutectic (E).

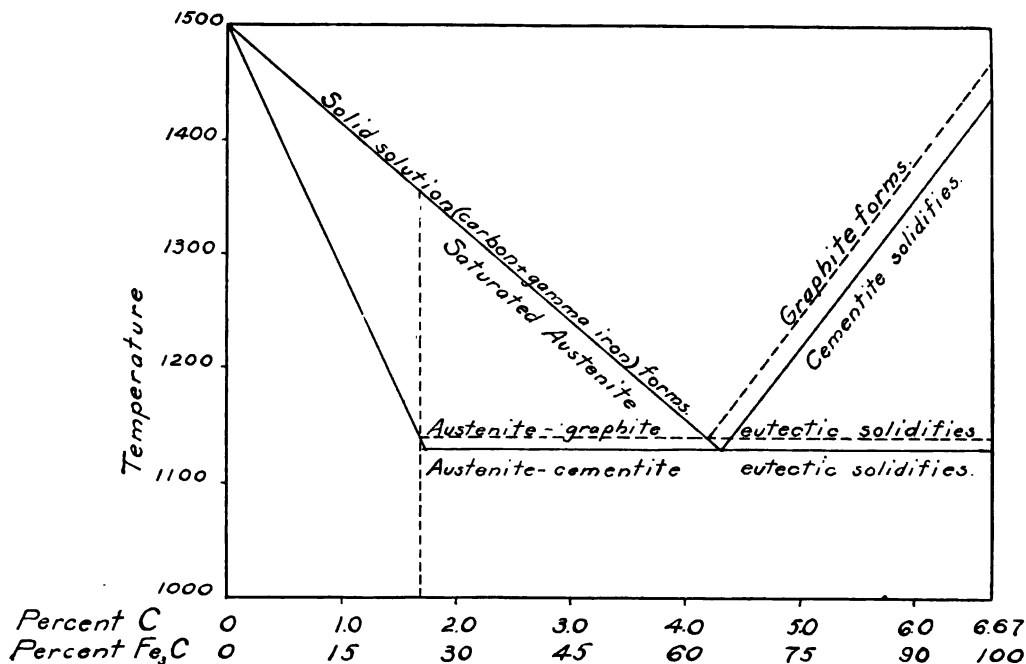


Fig. 415. — Combined graphite-cementite fusibility curves of iron-carbon alloys.

In the first instance the two following equations

$$(1) A + E = 100$$

$$(2) \frac{1.70}{100} A + \frac{4.3}{100} E = C$$

will give the values of A and E for any known carbon content (C) while in the latter case the equations

$$(1) Cm + E = 100$$

$$(2) \frac{6.67}{100} Cm + \frac{4.3}{100} E = C$$

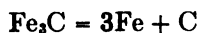
will likewise give the values of Cm and E.

An alloy, for instance, containing 3 per cent of carbon will be found to contain 50 per cent of eutectic and 50 per cent of saturated austenite, while an alloy with 5 per cent carbon is composed of 70.5 per cent of eutectic and 29.5 per cent free cementite.

Iron-Graphite Fusibility Curve.—It has already been mentioned that some writers claim that graphite instead of cementite may, and if time be given does, form on solidification; in other words, that the eutectic alloy may be composed of saturated austenite and graphite, and that free graphite may separate during the solidification of alloys containing more than 4.3 per cent carbon. The diagram interpreting this assumption which may be called the iron-graphite fusibility curve is shown in Figure 414. It will be seen to be similar to the iron-cementite diagram (Fig. 411).

Combined Graphite-Cementite Diagram.—Recognizing the possibility of the formation of a graphite-austenite eutectic and of a cementite-austenite eutectic according to the rate of cooling, some writers, notably Charpy and Grenet, Heyn, and Benedicks, recommend the use of double solidification curves in the equilibrium diagram of iron-carbon alloys. These double curves are shown in Figure 415, the dotted lines referring to the austenite-graphite system. It will be noted that free graphite and the graphite-austenite eutectic form respectively at temperatures slightly higher than those at which free cementite and the cementite-austenite eutectic form, the solidification of the latter constituents being regarded as due to surfusion or undercooling. It is accordingly believed that only the iron-graphite system is stable, the iron-cementite system being "metastable." Our reasons for believing that graphite and not cementite is the final condition to be assumed by carbon are based on repeated and concordant observations that any condition promoting stable equilibrium results in the transportation of cementite into graphite as, for instance, very slow cooling during and below solidification or long exposure of cementite (as in the manufacture of malleable cast-iron castings) to a high temperature, while on the contrary, treatments opposing equilibrium, such as quick cooling, always result in the formation or retention of cementite. Roozeboom, when he first took up the study of the iron-carbon diagram, believed that cementite was the final stable condition of carbon, any graphite having formed during solidification combining with iron at some 1000 degrees C. to form cementite. The error of this view soon became apparent, however, to Roozeboom himself.

Graphitizing of Cementite.—Although recognizing the fact that graphite and not cementite must be the final condition assumed by carbon, the author believes with some other observers that graphite never forms directly as iron-carbon alloys solidify, its occurrence always resulting from the breaking up of cementite according to the reaction



from which it would follow that the iron-graphite fusibility curve need not be included in the equilibrium diagram. Even those who believe in the possibility of the direct formation of graphite do not deny that cementite is the constituent which generally forms first on solidification; they state that the separation of graphite from molten iron is possible only in the case of very slow cooling. As a matter of fact, however, they offer no conclusive evidences that such separation ever takes place. From the formation of "kish," that is, of graphite floating on the surface of a ladleful of molten cast iron, it does not follow that such graphite formation was not preceded by the formation of cementite. If, on very slow cooling, graphite separated directly from molten iron, the bulk of it at least should rise to the top of the molten bath and the solidified mass should be found *much* richer in graphite near its surface than at some distance from it. The author does not understand such heterogeneity in the distribution of graphitic carbon to be observed in the case of gray cast-iron cast-

ings.¹ On the contrary, on the assumption that graphite results from the breaking up of cementite soon after its solidification, it is readily understood why, in spite of their very great difference in specific gravity, iron and graphite are found uniformly distributed in the various parts of castings. The microscopical examination of the structure of very slowly cooled castings does not reveal the existence of a graphite-austenite eutectic.

That cementite is unstable, being readily converted into iron and graphitic carbon, is also generally admitted. It is upon this instability of cementite that the important industrial operation of converting white cast-iron castings into graphitic malleable castings is based. And there is abundant evidence that the higher the temperature, the more readily is cementite dissociated, from which it follows that the higher the temperature at which cementite *forms* the more readily will it be converted into graphitic carbon. Bearing this in mind, and with the assistance of the diagram of Figure 413, let us look more closely into the graphitizing of cementite. The diagram shows clearly that, during the solidification of alloys containing more than 1.70 per cent of carbon, (1) some cementite forms as pro-eutectic cementite if the metal contains more than 4.3 per cent carbon, (2) some cementite forms as eutectic cementite in all alloys, (3) some cementite remains dissolved in the eutectic-austenite of all alloys, and (4) some cementite remains dissolved in the free austenite of alloys containing less than 4.3 per cent carbon. Considering first the free cementite, that is, the pro-eutectic and the eutectic cementite, it is evident that the former is formed at a higher temperature, and that the more carbon in the alloy the higher the temperature at which it begins to form. It seems safe to infer, therefore, that pro-eutectic cementite will break up into graphite and ferrite more readily than eutectic cementite, this being consistent with the well-known fact that hyper-eutectic alloys are generally rich in graphite even after relatively quick cooling. The presence of pro-eutectic cementite may also promote the formation of graphitic carbon because once this graphitizing process is started, it is likely to extend, if time be given, to the bulk of the cementite, first the eutectic cementite and later the austenite-cementite undergoing the change. Alloys containing less than 4.3 per cent carbon and consequently free from pro-eutectic cementite should not become graphitic as readily because of the lower temperature at which eutectic-cementite forms. If a large proportion of cementite be formed, however, that is, if the alloys contain more than 3 or 3.5 per cent of carbon, a certain amount of graphitizing is readily induced through slow cooling. With decreasing carbon the breaking up of cementite becomes progressively more difficult until, in alloys containing less than 1.7 per cent carbon (the steel series), and, therefore free from eutectic cementite, graphitic carbon is very seldom formed.

It should be borne in mind that while those alloys which contain but a small proportion of carbon cannot be made graphitic, when a large proportion of carbon is present, the graphitizing once started may be made to include the totality of the cementite, thus explaining the freedom of steel from graphite and the freedom of some cast irons from cementite.

The foregoing remarks apply to pure iron-carbon alloys, the influence of the elements generally present in commercial products having been purposely ignored. When dealing with commercial steel and cast iron, the well-known influence of silicon in promoting the formation of graphitic carbon should be remembered as well as the opposite influence of sulphur and manganese. Because of the presence of a notable

¹ Howe reports the segregation of graphite in the upper part of kish-bearing cast iron, but this is readily explained on the ground that such irons must be hyper-eutectic in composition and that the pro-eutectic cementite beginning to graphitize while the iron is still partially liquid shows a tendency to rise to the top, hence indeed the formation of kish.



Fig. 416. — Magnified 50 diameters.



Fig. 417. — Magnified 750 diameters.



Fig. 418. — Magnified 50 diameters.



Fig. 419. — Magnified 750 diameters.

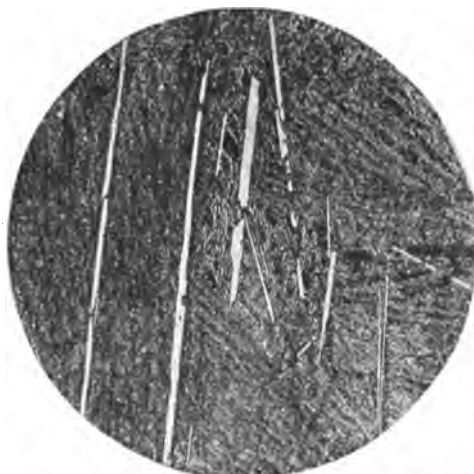


Fig. 420. — Magnified 50 diameters.



Fig. 421. — Magnified 750 diameters.

Figs. 416 and 417. — Iron-carbon alloy. Hypo-eutectic. Structure immediately after solidification. Dark crystallites of saturated austenite in a matrix of austenite-cementite eutectic. Figs. 418 and 419. — Iron-carbon alloy. Austenite-cementite eutectic. Figs. 420 and 421. — Iron-carbon alloy. Hyper-eutectic. Structure immediately after solidification. Needles of cementite in a matrix of austenite-cementite eutectic. (Görrens.)

proportion of silicon, commercial cast irons after slow cooling are necessarily more graphitic than pure alloys of same carbon content.

Structure of Iron-Carbon Alloys Immediately after Solidification. — If the alloy contains less than some 1.70 per cent carbon it is made up after complete solidification of crystalline grains of austenite. It has been explained, however, that in the absence of manganese or other “retarding” elements it is not possible to prevent, even through very rapid cooling, the transformation of some of the austenite at least into martensite. The polyhedral structure of austenite has been illustrated in these lessons in the case of special steels (manganese and nickel steels) and it is now well understood that the

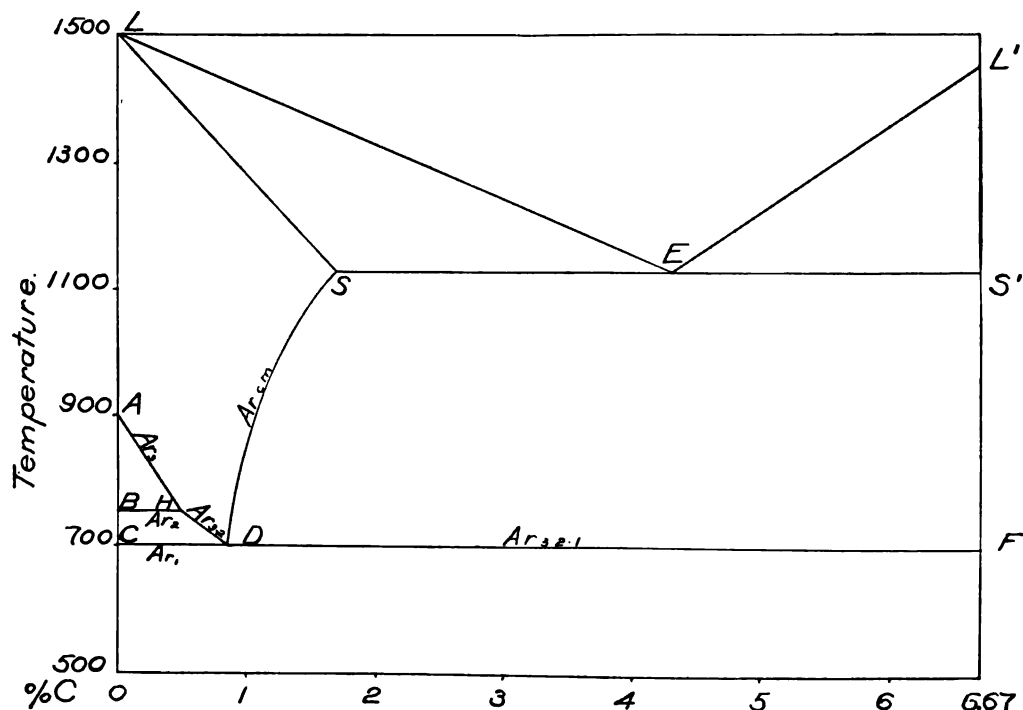


Fig. 422. — Equilibrium diagram of iron-carbon alloys.

frequent network structures of slowly cooled steel are due to the existence of polyhedral austenitic structures above their critical range.

If the alloy contains from 1.70 to 4.3 per cent carbon it is made up, after solidification, of crystals of saturated austenite and of eutectic alloy. This is well shown after Gørrens in Figure 416, in which the dark “pine tree” crystals consist of saturated austenite, while the ground mass is the cementite-austenite eutectic.¹ In Figure 417 the same structure is shown more highly magnified. If the alloy contains exactly 4.3 per cent carbon, it consists wholly of eutectic as shown under different magnifications in Figures 418 and 419. It has been seen that, theoretically, this eutectic contains 47.7 per cent of saturated austenite (the dark constituent), and 52.3 per cent of cementite. Alloys containing more than 4.3 per cent carbon consist after solidification of free cementite in the form of needles embedded in a eutectic matrix as shown in Figures 420 and 421.

It should be noted that the dark constituent occurring in these structures and described as saturated austenite may not be absolutely unaltered austenite because of

¹ Wüst has suggested the name of “Ledeburite” for this eutectic in honor of the late, well-known German metallurgist A. Ledebur.

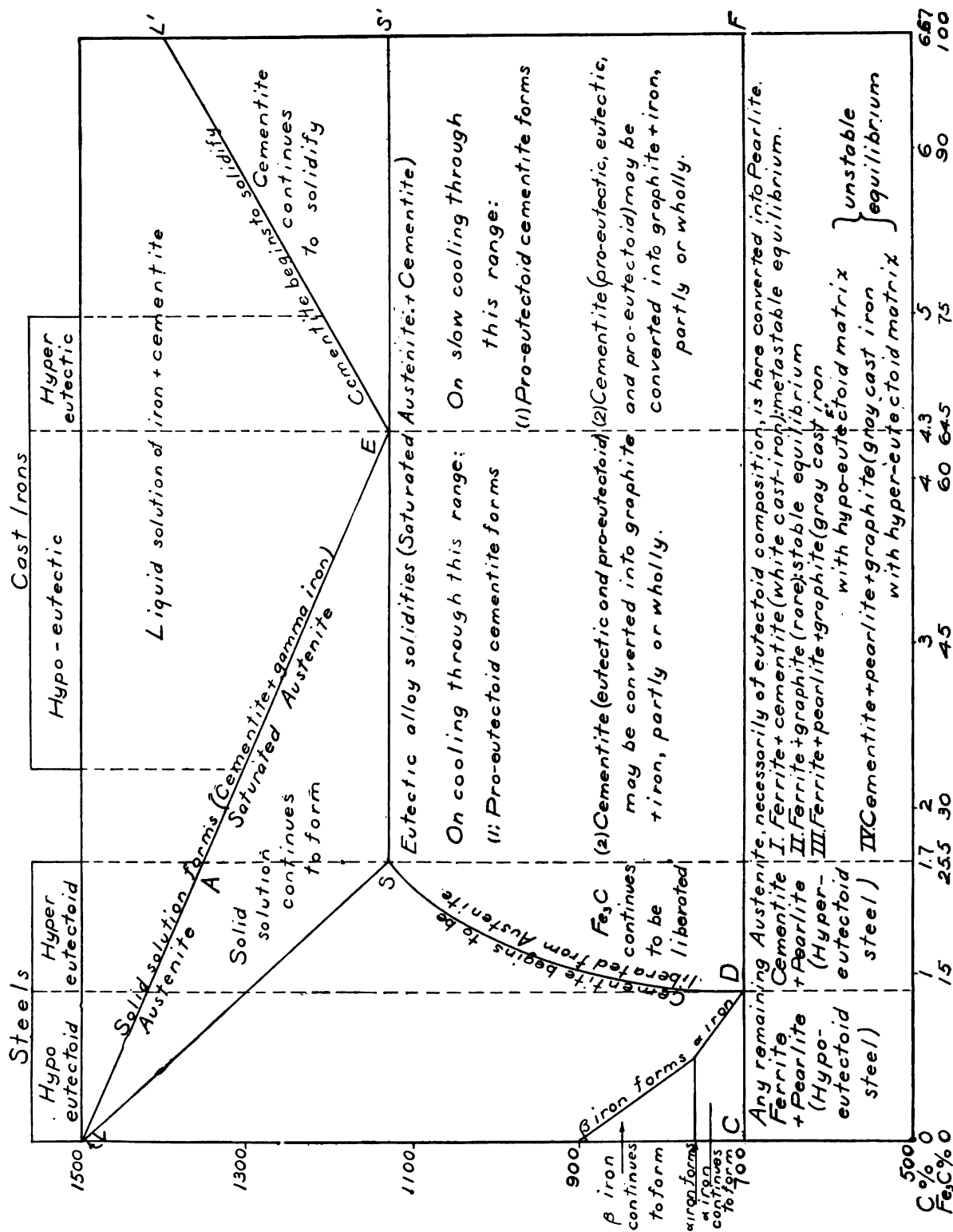


Fig. 423 — Equilibrium diagram of iron-carbon alloys with description.

the difficulty of completely preventing the transformation of that constituent even in the presence of a large amount of carbon and by very sudden cooling. If the austenite has undergone some transformation, however, so that it contains some martensite and even troostite those transformations must have taken place *in situ* and the structures reproduced in Figures 416 to 421 must represent accurately the structural aspect of the corresponding alloys after solidification.

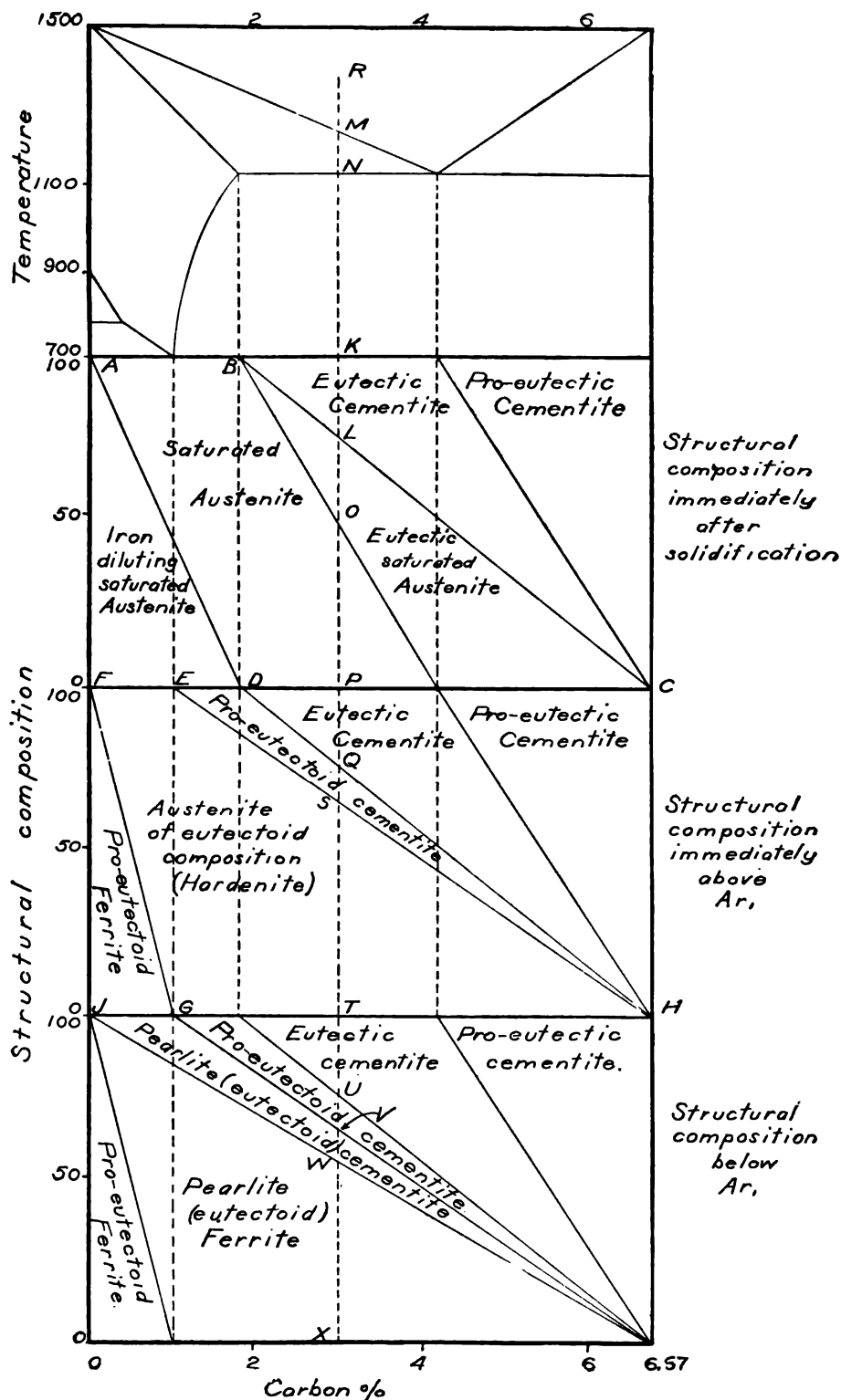
Complete Equilibrium Diagram. — In the foregoing pages only the solidification curves of iron-carbon alloys have been considered and the probable mechanism of their freezing explained. Their equilibrium diagram, however, must include all heat evolutions observed on cooling from the liquid condition to atmospheric temperature; in other words, the thermal critical points fully described in previous chapters are part of the complete equilibrium diagram as indicated in Figure 422.

Since the meaning of every curve of this diagram has been discussed, it only remains to inquire into any possible structural or other changes taking place *after* solidification and *before* the alloys reach their respective thermal critical point or points, that is, while they cool from the solidus LSS' to the eutectoid line CDF . The changes which do or may take place as the alloys cool in this range are clearly stated in Figure 423. In this diagram the most likely significance of every curve is indicated as well as the nature of all structural transformations, and of all possible resulting structures after complete cooling. The author believes that it embodies those inferences best supported by analogy and by experimental evidences. Although necessarily involving some repetition, a methodical examination of the various parts of this complete diagram seems advisable, as it will permit a recapitulation of the various matters previously discussed.

Let us consider (1) the solidification of iron-carbon alloys, (2) their cooling from the solidus $LSES'$ to the eutectoid temperature CDF , and (3) their cooling through the eutectoid temperature and their final structures.

According to the mechanism of their solidification iron-carbon alloys are divided into three classes, namely, (1) alloys containing less than 1.70 per cent of carbon, (2) alloys containing between 1.70 and 4.3 per cent carbon, and (3) alloys containing more than 4.3 per cent of carbon. Alloys containing less than 1.70 per cent of carbon and including, therefore, all the steels of commerce solidify as solid solutions of the carbide Fe_3C (cementite) in gamma iron, these solutions being known as austenite. LA is the liquidus and LS the solidus of these alloys. Alloys containing between 1.70 and 4.3 per cent of carbon solidify through the formation of crystals of saturated austenite at gradually decreasing temperatures and through the final solidification, at the eutectic temperature, of the residual molten metal necessarily of eutectic composition. Alloys containing more than 4.3 per cent of carbon solidify through the formation of cementite crystals at gradually decreasing temperatures, and through to final solidification, at the eutectic temperature, of the residual molten metal necessarily of eutectic composition.

In cooling below their solidus, LS , alloys with less than 1.70 per cent carbon undergo no change until they reach their thermal critical points Ar_3 , $Ar_{3.2}$, $Ar_{3.2.1}$ or Ar_{cm} as the case may be, when, if they contain less than some 0.85 per cent of carbon (hypo-eutectoid steels), some iron is set free and converted into beta iron, while if they contain more carbon (hyper-eutectoid steels), cementite is liberated. In either case when the eutectoid temperature is reached the residual austenite, now of eutectoid composition (0.85 per cent carbon), is converted into pearlite.



After solidification, alloys containing between 1.70 and 4.3 per cent carbon are aggregates of saturated austenite (austenite containing 1.70 per cent C or 25.5 per cent cementite) and of cementite-austenite eutectic. On cooling below their solidus, cementite (pro-eutectoid cementite) is liberated both from the free and from the eutectic-austenite, while if the cooling be sufficiently slow both the eutectic and pro-eutectoid cementite may be partly or wholly dissociated into graphite and iron (ferrite). Indeed, the graphitizing may even include the eutectoid cementite, in which case the alloy is made up solely of ferrite and graphite.

Alloys containing more than 4.3 per cent of carbon are, immediately after solidification, aggregates of cementite (pro-eutectic cementite) and of cementite-austenite eutectic. On slow cooling below their solidus, cementite (pro-eutectoid cementite) is liberated from the eutectic austenite while the pro-eutectic, eutectic, and pro-eutectoid

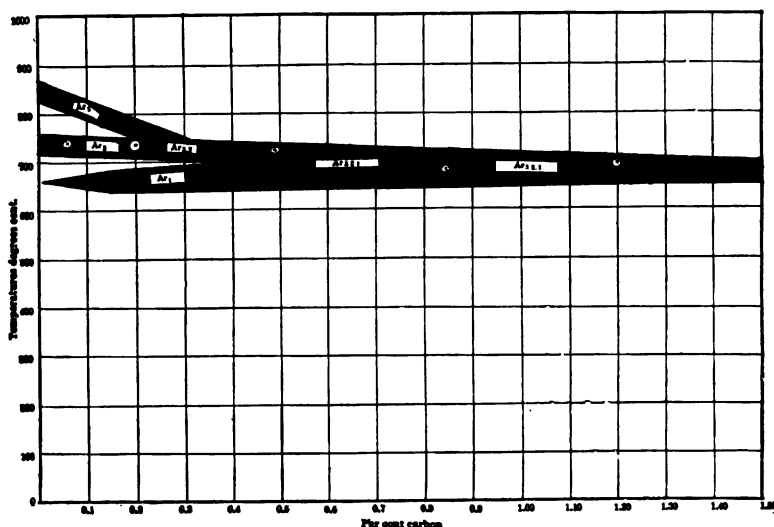


Fig. 425. — The author's early equilibrium diagram (1896).

cementite may be partly or wholly dissociated into graphite and ferrite, in some extreme cases the eutectoid cementite even being graphitized.

On cooling through the eutectoid temperature, any remaining austenite is bodily converted into pearlite.

The above consideration clearly shows that in alloys containing more than some 1.70 per cent carbon four types of structure may be formed according to the rate of cooling below the solidus:

(I) Cementite plus pearlite, the structure of white cast iron, readily produced by quick cooling and representing a metastable equilibrium. (II) Ferrite and graphite, an extreme case, possible only after very slow cooling and in the presence of much silicon, little manganese, and sulphur, and representing stable equilibrium. (III) Cementite plus pearlite and graphite, the structure of gray cast iron with hyper-eutectoid matrix, resulting from slow cooling, promoted by the presence of silicon and opposed by sulphur and manganese. (IV) Pearlite, ferrite, and graphite, the structure of gray cast iron with hypo-eutectoid matrix, produced because of slower cooling or because of the presence of more silicon or of less sulphur and manganese.

It will be explained in the next chapter that, according to the phase rule, only two components may be present in a binary alloy in a state of equilibrium from which it follows that gray cast irons, since they contain besides iron both cementite and graphite, are out of equilibrium. One of the components must disappear if the alloy is to assume equilibrium. Cementite is undoubtedly that component as proven by the malleablizing of cast iron when cementite is readily dissociated into graphite and ferrite on prolonged heating to a high temperature.

In Figure 424 the complete equilibrium diagram is shown combined with three constitutional diagrams showing graphically the structural composition of iron-carbon alloys (1) immediately after their solidification, (2) immediately before the eutectoid temperature, and (3) below the eutectoid temperature, *on the assumption that no graphitic carbon is formed*. The structural changes taking place while the alloys

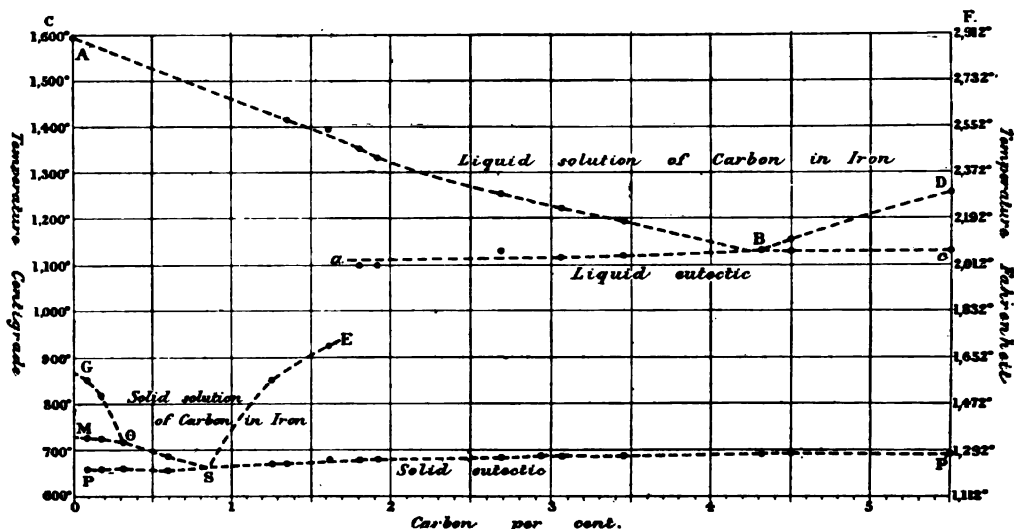


Fig. 426. — Roberts-Austen's first equilibrium diagram (1897).

cool below their solidus down to the eutectoid temperature are, in this way, clearly depicted. The following facts, for instance, are graphically shown, (1) the pro-eutectic cementite formed during the solidification of hyper-eutectic alloys and the eutectic cementite present in all alloys containing more than 1.70 per cent carbon remain unchanged as the alloy cools to atmospheric temperature, (2) the free saturated austenite of hypo-eutectic alloys, as well as the eutectic-austenite, are converted into eutectoid austenite through the liberation of cementite (pro-eutectoid cementite), the area *EDH* representing the cementite thus set free, and (3) in hypo-eutectoid alloys iron is set free as shown by the area *FJG*. The lower diagram shows that, in cooling through the eutectoid temperature, the remaining austenite, now necessarily of eutectoid composition, and sometimes called hardenite is converted into pearlite. Taking, for instance, the metal whose composition and temperature are represented by the point *R*, its transformations and final structure are clearly shown. At *M* it begins to solidify through the formation of crystals of saturated austenite; from *M* to *N* the austenite crystals continue to grow, the percentage of free austenite present in the solidified metal being represented by the distance *OP*; at *N* the residual bath

solidifies as a eutectic alloy, the percentage of which is proportional to the distance KO ; this eutectic contains $KL = PQ = TU$ per cent of cementite and LO per cent of saturated austenite; LP is the total amount of austenite in the alloy; after solidification in cooling from N to K , pro-eutectoid cementite is liberated both from the free and from the eutectic-austenite, QS representing the percentage of cementite finally expelled; on reaching the point K , the remaining austenite, ST , is of eutectoid composition, when it is sometimes called hardenite, and in cooling through K this austenite is converted into pearlite, the metal being finally made up of TU per cent of eutectic cementite, UV per cent of pro-eutectoid cementite, and VX per cent of pearlite, the latter containing VW per cent of cementite, and WX per cent of ferrite, or of TV per cent of free cementite and VX per cent of pearlite, or again of TW per cent of total cementite and WX per cent of ferrite.

Historical.—In view of the scientific and practical importance of the equilibrium

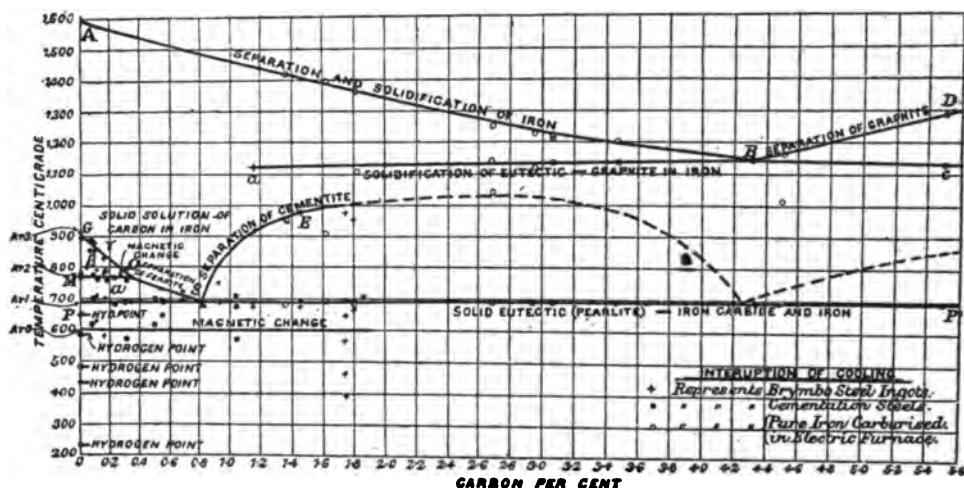


Fig. 427. — Roberts-Austen's second equilibrium diagram (1899).

diagram of iron-carbon alloys, a brief historical sketch of its evolution should be of interest to the reader. The first diagram was published by the author in 1896.¹ It is reproduced in Figure 425. It will be noted that, although the diagram includes only the thermal critical points, it is otherwise substantially accurate. In describing it the author wrote in part:

"Figure 1 shows graphically the position of the critical points in *cooling* steels of various carbons. The width of the black lines does not refer to the intensity of the retardations, but only indicates the range of temperature which they cover. For instance, it shows that the single retardation of high carbon steel begins at about 680 deg. C. and ends at about 640 deg. C. The maximum evolution of heat lies somewhere between these limits, but not necessarily in the middle.

"This graphical representation was obtained by plotting the results of the investigations of Osmond, Howe, Roberts-Austen, Arnold, and the writer; and, with one or two exceptions all their figures fall very nearly within the limits here indicated."

¹ "The Microstructure of Steel and the Current Theories of Hardening," ALBERT SAUVEUR, Transactions American Institute of Mining Engineers. 1896, p. 867.

It is from this modest beginning that the present diagram was evolved.¹

In 1897 Roberts-Austen published in his fourth report of the Alloys Research Committee of the Institution of Mechanical Engineers the diagram reproduced in Fig. 426.

Two years later, in 1899, the diagram shown in Fig. 427 was published by Roberts-Austen and Stansfeld in the fifth report of the Alloys Research Committee. Some of the conspicuous features of this diagram should be noted. The solidification point of pure iron was indicated to be 1600 degrees C. whereas we know now that it is nearly 1500 deg. No attempt had been made yet at ascertaining the end of the solidification, that is, the solidus, of alloys forming solid solutions; the formation of a eutectic on solidification was indicated as taking place in alloys containing more than one per cent carbon; graphite was supposed to crystallize during the solidification of alloys con-

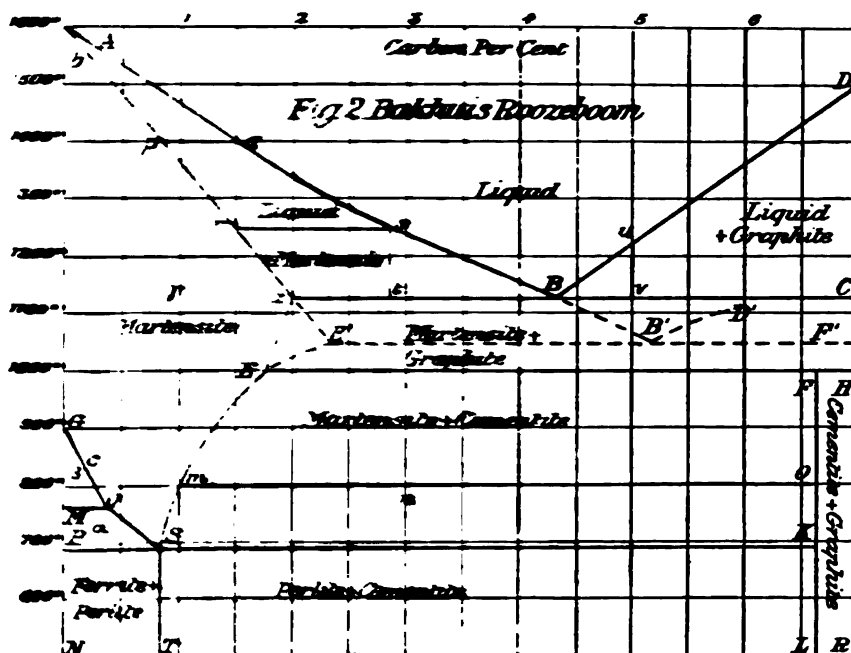


Fig. 28. - Roozeboom's equilibrium diagram (1900).

taining more than 4.3 per cent carbon, there being in the diagram no indications of possible formation of cementite; the eutectic alloy was assumed to be a graphite-iron eutectic; critical points occurring below the eutectoid temperature were represented in the diagram and marked "hydrogen points" (see Chapter X, "Minor Critical Points"); the A_{cm} curve was arbitrarily extended to yield a V-shaped curve. Roberts-Austen mentioned the formation of a solid solution, free in hypo-eutectic steels, and as a constituent of the eutectic in alloys of eutectic composition, and he ascribed the presence of free cementite in cast iron to the liberation of that constituent from solid solution.

In 1900 Roozeboom took up the study of Roberts-Austen's diagram, and applying to it the teachings of the phase rule published the diagram of Fig. 428 as a probably accurate representation of the solidification mechanism of iron-carbon alloys and of the structural transformations taking place after solidification. In this diagram, the line ba , that is, the solidus of alloys forming solid solutions, is for the first time indicated;

¹ Since these remarks were written Prof. H. M. Howe has expressed the opinion that credit for first equilibrium diagram is due to Reinhard Mannesmann.

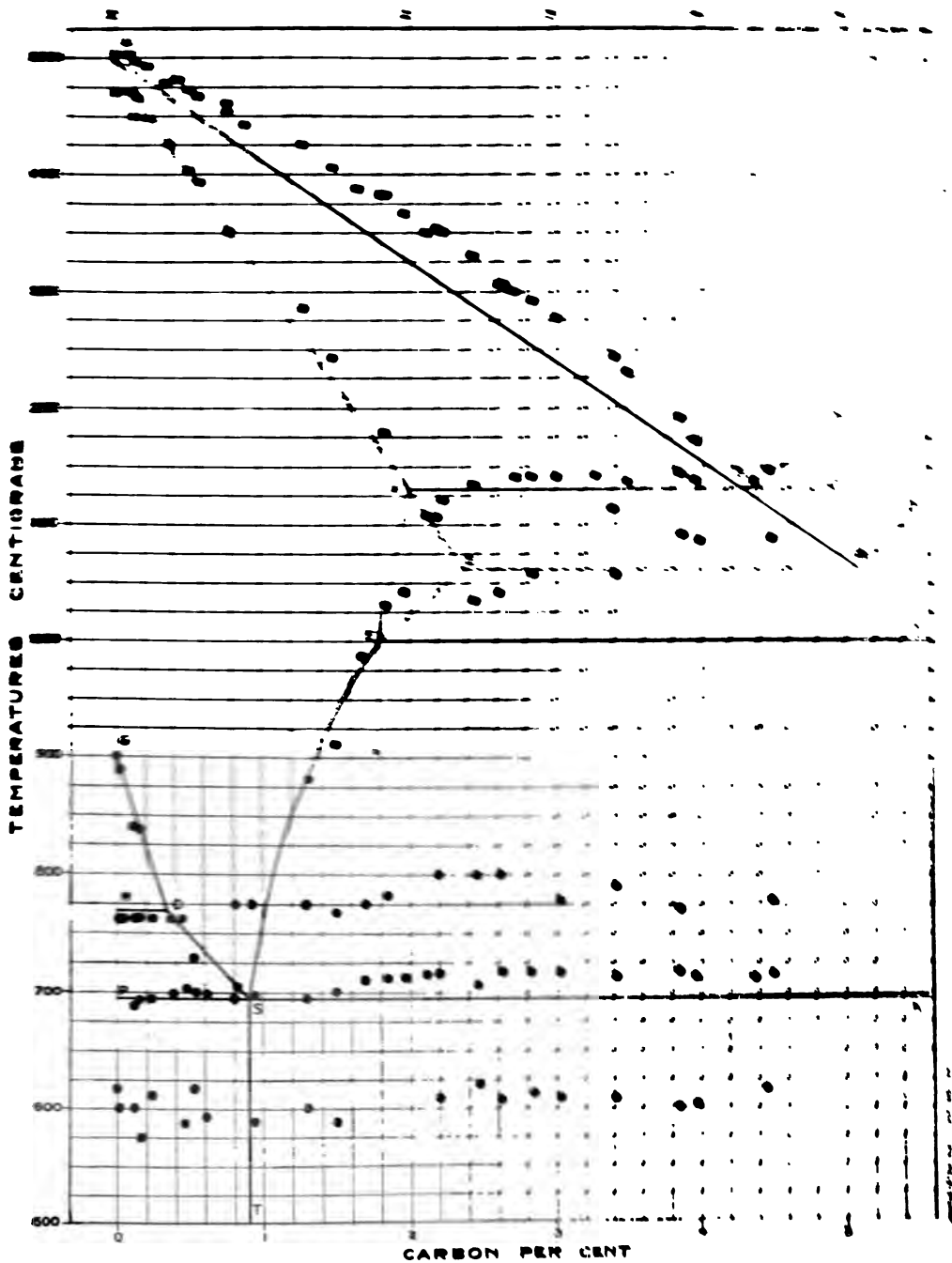


Fig. 429. — Carpenter's and Keeling's equilibrium diagram (1904).

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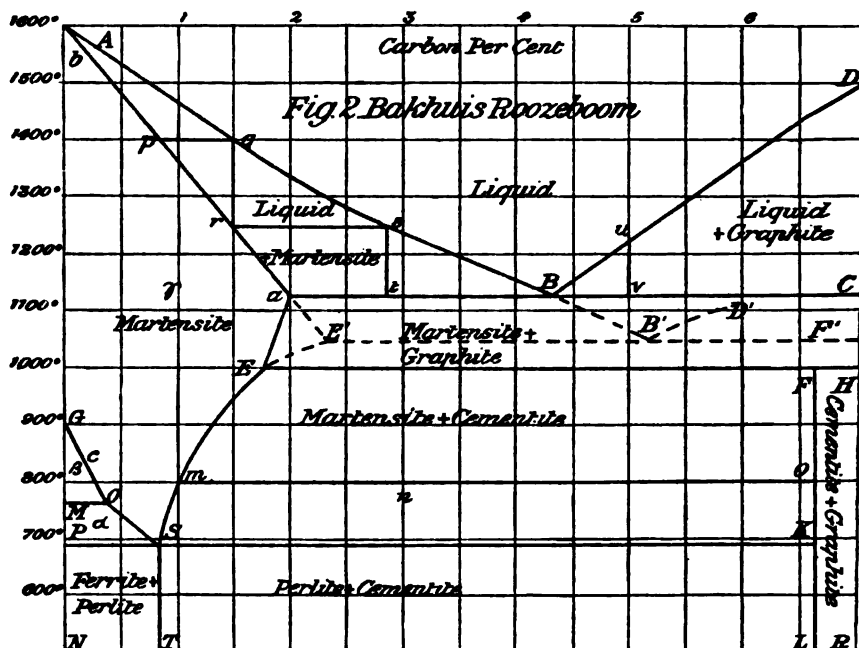


Fig. 428. — Roozeboom's equilibrium diagram (1900).

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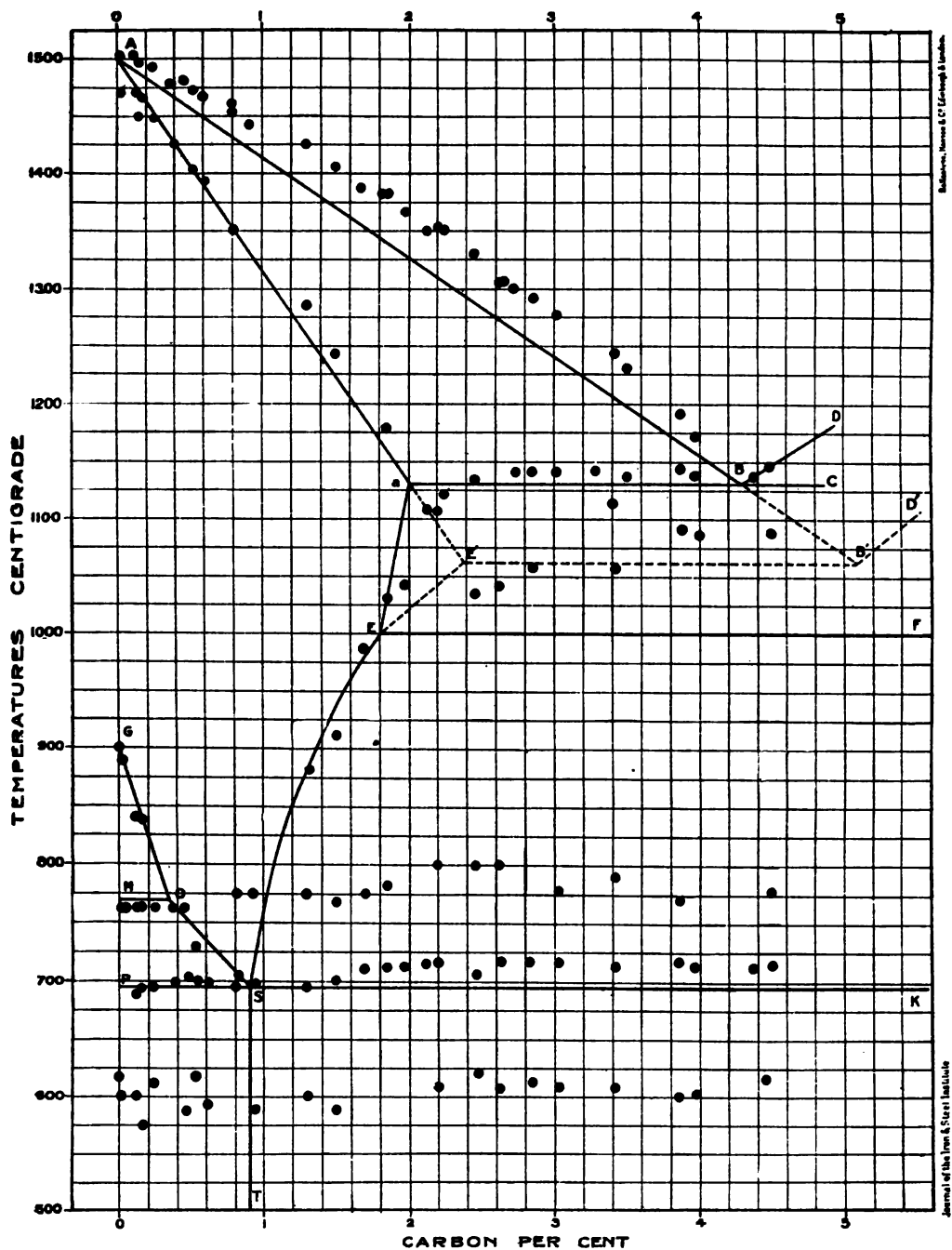


Fig. 429. — Carpenter's and Keeling's equilibrium diagram (1904).

the word martensite is used instead of austenite to denote the solid solution of iron and carbon; free graphite is assumed to form during the solidification of alloys containing more than 4.3 per cent carbon and the constituents of the eutectic alloy are supposed to be martensite (solid solution) and graphite. The Ar_{cm} curve of hyper-eutectoid steels is arbitrarily extended as an horizontal line starting from E (1.75 per cent carbon and 1000 deg. C.) and extending to the end of the diagram. Roozeboom argued that, while graphite formed on solidification in all alloys containing more than 2 per cent carbon, this graphite at 1000 deg. (line EF) recombined with iron to yield cementite so that, finally, alloys in equilibrium would contain only ferrite and cementite, thus conforming to the phase rule which forbids the presence of more than two components in binary alloys. It has since been conclusively shown that Roozeboom was in error, that while the ferrite-cementite system is in equilibrium according to the

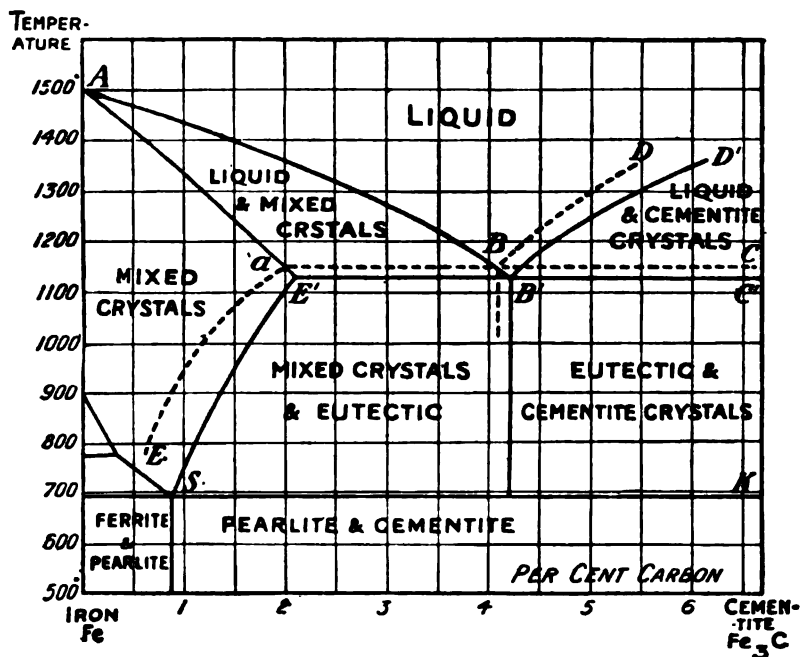


Fig. 430. — Benedicks' double equilibrium diagram.

phase rule, it is in metastable equilibrium, the ferrite-graphite system being the only stable one. The hypothetical horizontal line EF is now consequently omitted from the equilibrium diagram, and the Ar_{cm} curve made to join the eutectic line at its origin (a).

In 1904 Carpenter and Keeling made a series of very careful experiments in order to ascertain the evolutions of heat taking place in cooling pure iron-carbon alloys from the liquid state to atmospheric temperature. By plotting their results, the equilibrium diagram reproduced in Figure 429 was obtained. The solidification of pure iron is shown to take place at 1500 deg. C. The curves are otherwise identical to those of Roozeboom, the horizontal line EF having been introduced. The faint evolutions of heat occurring in the vicinity of 600 deg. C. already discovered by Roberts-Austen and ascribed by him to the presence of hydrogen, were also observed by Carpenter and Keeling, as well as some faint evolutions in the vicinity of 775 deg., the meaning of which remains uncertain.

When it became apparent that graphite and not cementite must be the final stable form of carbon, several authorities argued that two equilibrium conditions could exist according to the rate of cooling during solidification, one of them stable, the other metastable, and that this should be indicated in the diagram. This view was presented notably by Charpy and Grenet, by Benedicks and by Heyn. The double diagram advocated by them is represented in Figure 430. The solidification of free cementite and of the cementite-austenite eutectic being assumed to be due to the well-known phenomenon of surfusion or undercooling, the corresponding curves are arbitrarily outlined at temperatures slightly lower than those pertaining to the formation of free

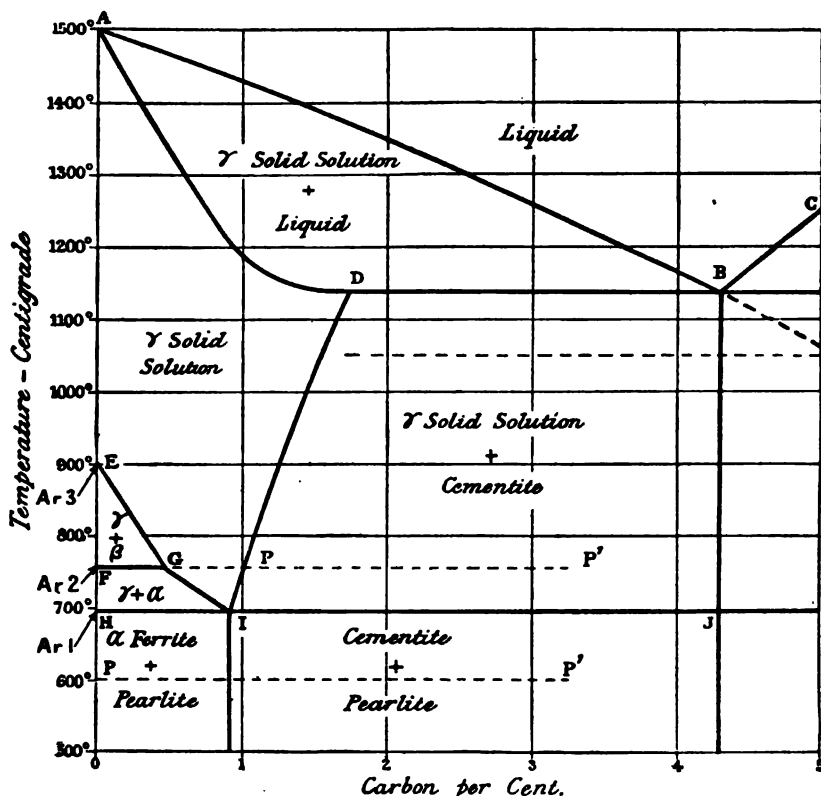


Fig. 431. — Rosenhain's equilibrium diagram (1911).

graphite and of graphite-austenite eutectic. The author has already shown why, in his opinion, the graphite curves should be left out. The view that cementite always forms during the solidification of iron-carbon alloys but that being unstable it is readily dissociated into ferrite and graphite, seems to be better supported by experimental evidences and more consistent with practical facts.

Rosenhain has recently plotted the experimental results of Carpenter and Keeling, of Gutowsky and of himself, obtaining the diagram reproduced in Figure 431. He considers Gutowsky's results in regard to the form of the solidus curve of alloys forming solid solutions as more accurate than those previously published, and he incorporates them in the diagram as shown in Fig. 431, the solidus line being rounded instead of straight as heretofore represented. In justification of his course, Rosenhain writes:

"We have now to consider the curved portion of the 'solidus,' the line *AD*. This

represents the temperatures at which the alloys have just completed their freezing process, that is, have just become completely solid, or, conversely, it represents the temperature of incipient fusion on heating. In the earlier investigations, and even in those of Messrs. Carpenter and Keeling, these temperatures were obtained by estimating the point on each of the cooling-curves where the heat-evolution due to solidification came to an end. Unfortunately, the *end* of a heat-evolution is never sharply indicated on the curves, so that this estimation was admittedly vague. Quite recently that determination has been repeated, and with considerable greater accuracy, because a very much more satisfactory method was available . . .

"The method of determining the 'solidus' was to take small pieces of steel, of known composition, heat them, and suddenly cool them from successively higher temperatures; afterward each specimen was examined by means of the microscope.

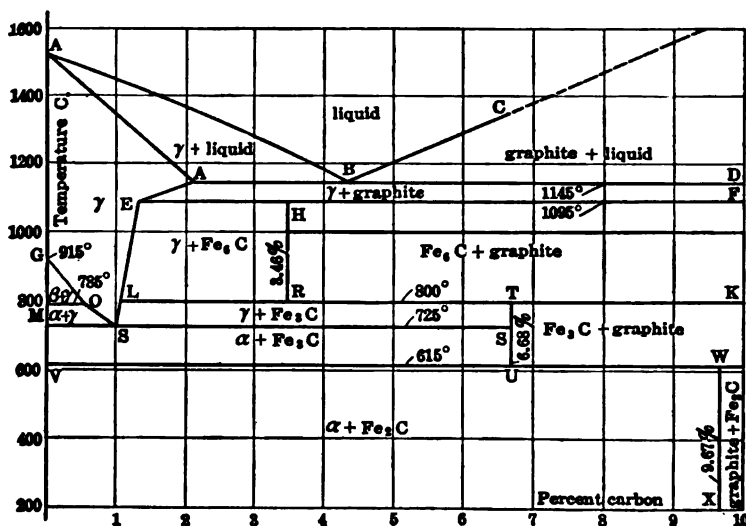


Fig. 432. — Upton's equilibrium diagram.

It is easy, as the photographs show, to determine what is the particular point at which you have reached a temperature where there was a small quantity of liquid metal present at the moment of quenching."

Upton's Diagram. — The rather revolutionary diagram shown in Figure 432 has been proposed by G. B. Upton. He considers it more satisfactory than the double diagram, as it does away with the necessary conception of a metastable and a stable equilibrium at nearly the same temperature. Upton argues that cementite decomposes above 800 deg. C. into graphite and iron, but that even after prolonged annealing some 3.5 per cent carbon remains combined from which it is inferred that the carbide Fe_3C forms (carbon 3.46 per cent) stable in the region *LEFK* in the diagram although he adds that it might be a solid solution containing that amount of carbon which forms at about 800 deg. Fe_3C is claimed to be converted into Fe_2C thus accounting for the evolutions of heat in this region reported by Carpenter and Keeling. At about 600 deg. according to the diagram Fe_3C is converted into Fe_2C thus explaining the evolutions of heat detected at that temperature by many observers. It is very difficult to accept the hypothesis that graphite is not the stable condition of

carbon in the area *LEHR* and that Fe_2C and not Fe_3C is the condition of the carbon remaining combined after complete slow cooling. The existence of both Fe_3C and Fe_2C is based on chemical tests the significance of which is far from evident. Justification for the line *EF* is claimed on the ground that evolutions of heat have been reported by Carpenter and Keeling as occurring at 1050 to 1100 deg. Other observers, however, have generally failed to detect these retardations. There are

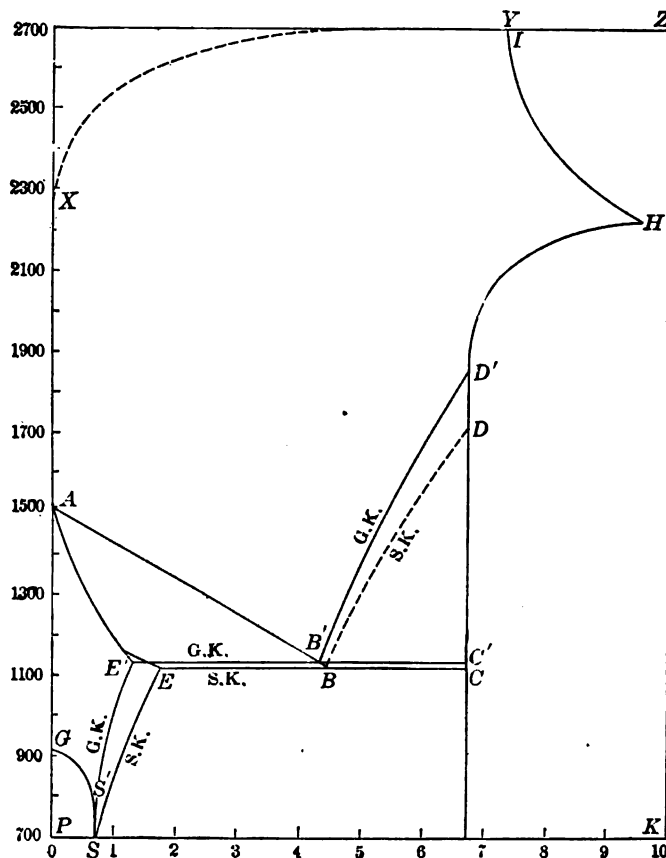


Fig. 433. — Ruff's equilibrium diagram.

other serious objections to Upton's diagram and its construction is so highly speculative as to render its closer study inadvisable in these pages.

Ruff's Diagram. — Professor Ruff has published the equilibrium diagram reproduced in Figure 433, which, it will be noted, is of the double type, *GK* representing equilibrium with graphite and *SK* with cementite. The diagram does not extend below the eutectoid line *PK* but includes alloys containing as much as 10 per cent carbon. The line *D'H* indicates the increasing solubility of carbon in iron with increasing temperature. At some 2200 deg. C. molten iron saturated with carbon contains nearly 10 per cent of that element. At this temperature Ruff believes that the alloy consists of the carbide Fe_2C as explained in Chapter XXII. As the temperature increases above 2200 deg. the solving power of iron for carbon decreases as

indicated by the line *HI*, carbon being rejected, probably through the breaking up of some Fe_2C into iron and graphite (see Chapter XXII). At some 2700 deg. iron can retain but a little over 7 per cent of carbon in solution. In cooling below 2200 deg. (line *HD'*) graphite and Fe_3C are formed from the transformation of Fe_2C ($3 \text{ Fe}_2\text{C} = 2 \text{ Fe}_3\text{C} + \text{C}$).

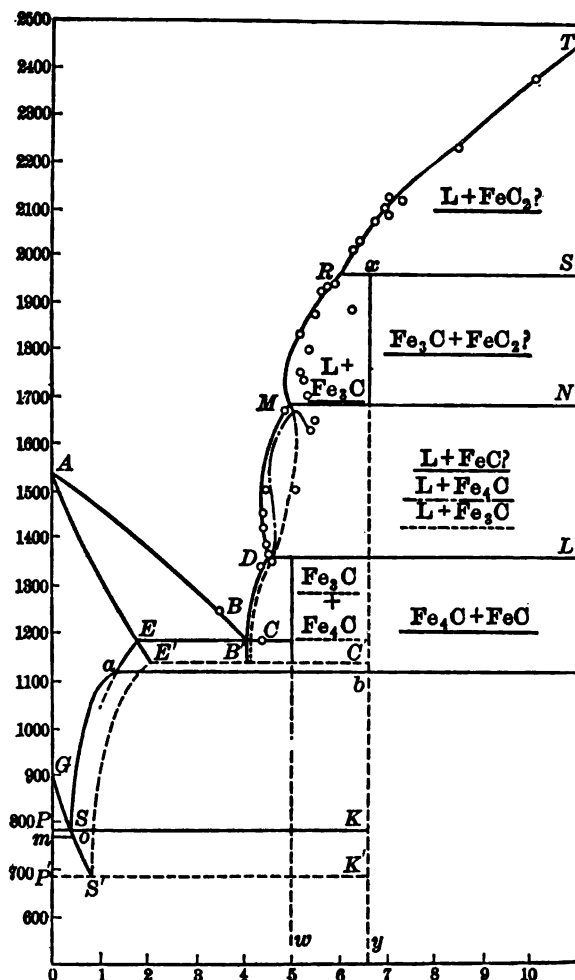


Fig. 434.—Wittorff's equilibrium diagram.

Wittorff's Diagram.—N. M. Wittorff worked out the diagram reproduced in Figure 434. It will be noted that (1) starting with an alloy containing some 11 per cent carbon, as it cools from T to R, that is, from some 2400 to 2000 deg. C. the carbide FeC_2 crystallizes out according to the diagram, (2) between R and M (2000 to 1700 deg.) Fe_3C forms through the transformation of some FeC_2 (3) between M and D (1700 to 1350 deg.) both FeC and Fe_4C are formed necessarily at the expense of FeC_2 which disappears and possibly also through the transformation of some of the Fe_3C , and (4) below D (1350 deg.) the liquid phase disappears.

Investigations of a region of the equilibrium diagram but little explored should be welcomed but in view of the fact that the experimental results of the different observers as well as the conclusions based upon them are at such variance, it seems advisable to omit from these pages a closer scrutiny of these recent diagrams. When some of the points that need clearing up have been settled the matter involved will be duly incorporated in a subsequent edition of this treatise.

CHAPTER XXVII

THE PHASE RULE

The Phase Rule to which references have been made in the preceding chapters should now be considered as it has been found of much assistance in interpreting correctly the iron-carbon equilibrium diagram.

Enunciation of the Phase Rule. — The phase rule was enunciated in 1878 by Willard Gibbs, at the time Professor of Physics in Yale University. It is one of the most notable contributions ever made to physical chemistry.

The phase rule deals with the *equilibrium* of systems and is generally expressed by the formula:

$$F = C + 2 - P$$

showing the relation existing between the *degrees of freedom* (F) of a *system*, the number of *components* (C), and the number of *phases* (P); it tells us that the number of degrees of freedom of any system is equal to the number of its components plus two, minus the number of phases present. In order to understand the phase rule and its application, it is necessary and sufficient to have an accurate understanding of the meaning of the terms employed in its enunciation, namely, equilibrium, degrees of freedom, components, and phases.

Equilibrium. — A substance or system may be said to be in a state of equilibrium when it is chemically and physically at rest, meaning by chemical rest that chemical compounds are neither being dissociated nor formed, and by physical rest, not the absence of motion but the absence of molecular transformation, such as changes of state or allotropic changes. It is necessary, however, to distinguish between *homogeneous* and *heterogeneous* substances. A substance is said to be homogeneous when it is chemically and physically uniform throughout, i.e. when any two portions of it possess identical chemical and physical properties. Homogeneous substances are necessarily gaseous mixtures, elements, chemical compounds, or liquid and solid solutions. The equilibrium of a homogeneous system is sometimes called homogeneous equilibrium. A heterogeneous substance is made up of two or more physically separate parts, that is, of parts having different physical properties. Ice and water, many rocks, and many alloys are instances of heterogeneous substances. If the component parts of heterogeneous substances may be present in indefinite proportions, the substances are mechanical mixtures; if they occur in definite proportions, the substances are eutectic or eutectoid alloys. The equilibrium of heterogeneous systems is sometimes called heterogeneous equilibrium.

Howe has recently suggested that the homogeneous constituents of alloys be called "metarals" because of the great analogy between the constitution of metallic alloys and of rocks, the minerals being the homogeneous components of the latter, while the word aggregate is very frequently used to designate heterogeneous alloys. In metal-

lography, therefore, metarals and aggregates may conveniently replace the equivalent terms, homogeneous and heterogeneous substances, of the physical chemist.

Only three independently variable factors can affect the equilibrium of a system, namely, (1) the temperature, (2) the pressure, and (3) the concentration or composition. If arbitrary values may be given to one or more of these factors without destroying the chemical and physical rest of the system, its equilibrium is said to be *stable*. On the contrary, if a change in value of any one of these three factors results in chemical or physical transformation, i.e. in atomic or molecular activity such as dissociation or formation of chemical compounds, changes of state, or allotropic changes, the equilibrium of the system was *unstable*. Water under atmospheric pressure is in stable equilibrium, for we may change its temperature within wide limits without causing it to undergo a change of state, while of course its chemical composition remains likewise unaffected. All elements are generally in a state of stable equilibrium, as well as an infinite number of substances composed of two or more elements, for they may be heated, for instance, through wide ranges of temperatures without upsetting their physico-chemical equilibrium. Examples of unstable equilibrium, however, are far from uncommon. During the solidification of substances, for instance, stages must generally be passed through during which the equilibrium of the substance is unstable, and it is often possible through very rapid cooling to retain in the cold the unstable conditions, because of the rigidity of the substance now opposing the changes needed for a return to stable equilibrium. It has been seen in these chapters that hardened steel is, for the above reason, unstable, hence the possibility of tempering it by slight reheating.

The kind of equilibrium known as *metastable* remains to be described. Liquids may be cooled, when taking the necessary precautions, below their normal freezing-point, without freezing, the phenomenon being known as superfusion, surfusion, or undercooling, and the substance being said to be in metastable equilibrium. Water, for instance, may be cooled below 0 deg. C. and still remain liquid. The introduction of a solid fragment of the substance, a piece of ice in the case of water, results in the solidification of the liquid while its temperature rises to its normal freezing-point. Otherwise, the substance may be kept liquid below its solidification point for any length of time. If the temperature of the liquid continues to fall, however, a point is reached when its equilibrium becomes *unstable*, i.e. when further lowering of temperature causes the liquid to solidify. To state the case broadly, the failure on the part of a system to undergo a certain chemical or physical transformation when that transformation is due, *although given the necessary time*, results in metastable equilibrium, while its failure to undergo a transformation *because of the necessary time being denied*, as in quenching, results in unstable equilibrium. Metastable equilibrium is stable, at least within narrow limits of temperature, while, theoretically at least, slight heating of a substance in unstable equilibrium should result in a partial return to a more stable condition, that is, in a partial occurrence of the transformation that was suppressed by quick cooling.

Degrees of Freedom. — By the degrees of freedom (sometimes called degrees of liberty), of a system is meant the number of the three independently variable factors, temperature, pressure, and concentration, which may arbitrarily be made to vary without disturbing the system's physico-chemical rest. It has already been noted that a system, in order to be in stable equilibrium, must have at least one degree of freedom. It will also be understood that no system can have more than two degrees of freedom because in the case of arbitrary values being given to two of the factors, the

value of the third is necessarily fixed, this being due to the known rigid relations existing between temperature, pressure, and concentration.

Systems which have no degree of freedom are said to be "unvariant" or "non-variant." Their equilibrium is necessarily unstable. Systems having one degree of freedom are called "univariant" or "monovariant," and those with two degrees of freedom "bivariant" or "divariant."

Phases. — By the phases of a system are meant the *homogeneous*, physically distinguishable, and mechanically separable constituents of that system. Water and ice, for instance, are possible phases of the water-ice system; quartz, feldspar, and mica are phases of granite, that is, of the silica-alumina-potash system. It will be apparent that phases must necessarily be gaseous mixtures, elements, definite chemical compounds, or solutions. As previously mentioned, Howe, following the petrographical nomenclature, and noting that the minerals are the phases of rocks, calls "metarals" the phases of metals and alloys.

Components. — The components of a system are described by Findlay as "those constituents the concentration of which can undergo *independent* variation in the different phases," by Bancroft as "substances of independently variable concentration," by Mellor as those "entities which are undecomposable under the conditions of experiments," by Howe as "free elements and those compounds which in the nature of the case are undecomposable under the conditions contemplated, and so play the part of elements." The components of a system may be either chemical compounds or elements, but there is at times some difficulty in grasping the distinction between the components of a system and its ultimate chemical constituents. The criterion by which to decide whether an entity is or is not a component, is the possibility of independent variation in the different phases. Take the system water, for instance: evidently water and not hydrogen and oxygen is the component, because any variation in the proportion of hydrogen would necessarily imply a corresponding and well-defined variation in the proportion of oxygen and vice versa. Findlay writes:

"In deciding the number of components in any given system, not only must the constituents chosen be capable of independent variation, but a further restriction is imposed, and we obtain the following rule: *As the components of a system there are to be chosen the **smallest number** of independently variable constituents by means of which the composition of each phase participating in the state of equilibrium can be expressed in the form of a chemical equation.*"

In the case of alloys, however, such difficulty does not arise, for the constituent metals are always the components of the systems.

The Phase Rule Applied to Alloys. — In dealing with alloys we may for all practical purposes ignore the influence of pressure, seeing that because of their feeble volatility they are practically always subjected to atmospheric pressure. Omitting the influence of pressure necessarily reduces by one the possible number of degrees of freedom so that in the case of alloys the phase rule may be expressed by the formula:

$$F = C + 1 - P$$

signifying that the number of degrees of freedom is equal to the number of components plus one, minus the number of phases. Since to be in stable equilibrium a system must have at least one degree of freedom, it is obvious that an alloy made up of n metals cannot have more than n phases. If it had $n + 1$ phases it would have no degree of freedom, that is, its equilibrium would be unstable. With $n - 1$ phases it would have

two degrees of freedom. It could not have less than $n - 1$ phases, since it cannot have more than two degrees of freedom.

The Phase Rule Applied to Pure Metals. — Pure metals have only one component, but their possible phases are (1) liquid metal, (2) solid metal, (3) several allotropic conditions of the solid metal. Let us consider Figure 435, which represents the solidification of a pure metal as explained in Chapter XXV.

Above the temperature T the metal is entirely liquid; it has but one phase, and consequently one degree of freedom ($F = 1 + 1 - 1 = 1$). The system above T is univariant; its temperature may be altered within wide limits without disturbing its

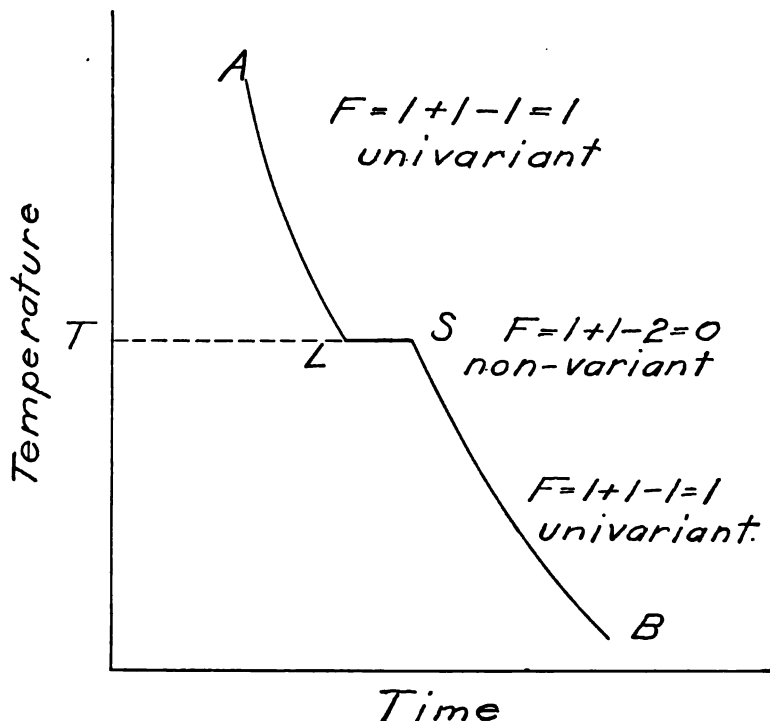


Fig. 435. — Equilibrium of pure metals according to the Phase Rule.

equilibrium: it remains liquid. At the temperature T two phases are present, solid metal and liquid metal, the metal having, therefore, no degree of freedom ($F = 1 + 1 - 2 = 0$): it is non-variant. Liquid and solid metal can exist only at one temperature, the critical temperature of solidification, any change of its temperature resulting in the disappearance of one of the phases, that is, in a return to stable equilibrium. Increasing the temperature must result in the disappearance of the solid phase, while lowering the temperature must cause the disappearance of the liquid phase. Below the temperature T the system contains only the solid phase, being, therefore, univariant: its temperature may be varied arbitrarily.

The Phase Rule Applied to Binary Alloys. — Binary alloys having for components the two alloying metals, the formula of the phase rule becomes:

$$F = 2 + 1 - P$$

$$\text{or } F = 3 - P$$

Clearly binary alloys when in a condition of stable equilibrium cannot have more than two phases. With one phase they will be bivariant, with two phases univariant, and with three phases non-variant. Let us apply the rule to the fusibility curves of binary alloys of metals partially soluble in each other when solid (Fig. 436). Above the liquidus MEM' there is but one phase present, namely the liquid phase, the system being, therefore, bivariant ($F = 3 - 1 = 2$), i.e. both temperature and concentration may be varied arbitrarily without upsetting the equilibrium of the system, which means, in the case under consideration, without causing its solidification. On reaching any point L of the liquidus the alloy begins to solidify, and two phases are now present, namely, solid solution and liquid alloy, the system becomes univariant ($F = 3 - 2 = 1$). Having but one degree of freedom only the temperature or the concentration may be

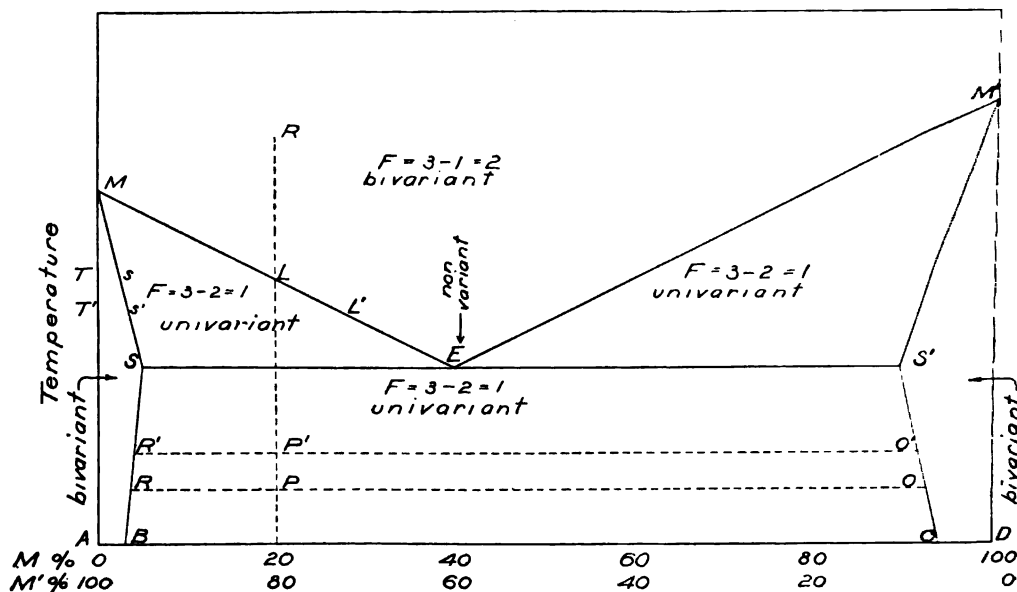


Fig. 436. — Equilibrium according to the Phase Rule of binary alloys whose component metals are partially soluble in each other in the solid state.

arbitrarily varied. Should we, for instance, lower the temperature of alloy R from T to T' (Fig. 436) the composition of the liquid phase necessarily shifts from L to L' , and that of the solid phase in equilibrium with it from s to s' . In the region $MS'S'M'$ of the diagram bounded by the liquidus and solidus lines, therefore, the alloys are univariant, any arbitrary change of temperature resulting in a well-defined change of concentration and vice versa. At E , corresponding to eutectic composition and eutectic temperature, three phases are present, namely two solid solutions and liquid alloy, the system having no degree of freedom ($F = 3 - 3 = 0$). Neither the temperature nor the concentration may be altered without causing the disappearance of at least one of the phases. Increasing the temperature must result in the disappearance of both solid solutions, the system becoming bivariant, while lowering it must be followed by the disappearance of the liquid phase. Again, shifting the concentration to the left or right of E must yield the univariant system solid solution plus liquid. Clearly two solid phases and a liquid phase can only exist at one critical temperature and for one critical composition of the alloy; in the case of a eutectic

alloy these three phases can exist only at its freezing temperature. In the areas *AMSB* and *DM'S'C* single homogeneous solid solutions only are present, that is, but one phase exists, and the corresponding alloys have, therefore, two degrees of freedom. Arbitrary changes both of temperature and composition within these areas do not disturb the equilibrium of the system. Within the region *BSS'C* two phases occur, solid solution *M* and solid solution *M'*, the corresponding alloys having, therefore, but one degree of freedom. Increasing the temperature from *P* to *P'*, for instance, must result in shifting the composition of the solid solutions respectively from *R* to *R'* and from *O* to *O'*.

The Phase Rule Applied to Iron-Carbon Alloys. — Since iron-carbon alloys belong to the class of binary alloys the constituents of which are partially soluble in each other in the cold, the application of the phase rule to their equilibrium diagram should not present any difficulty, but we have now to consider allotropic changes as well as changes of state. Their possible phases or metarals are: (1) liquid iron, (2) liquid solution of carbon (or Fe_3C) in iron, (3) solid solution (austenite) of carbon (or Fe_3C) in gamma iron, (4) solid gamma iron, (5) solid beta iron, (6) solid alpha iron (ferrite), (7) solid solution (martensite)¹ of carbon (or Fe_3C) in beta iron, (8) solid cementite, (9) graphite, and possibly others. The exact nature of troostite and sorbite being still in doubt, they are not here classified as phases, seeing that they may be, and probably are, aggregates of two or more phases, unless indeed they be, according to Benedicks, emulsions or colloidal solutions. Scientists do not agree, however, as to whether colloidal solutions are or are not phases, opinions differing in regard to their homogeneity. Indeed some writers like Le Chatelier question the existence of colloidal solutions which they consider as finely divided aggregates. Pearlite evidently is not a phase, but an aggregate of the two phases, ferrite and cementite, in constant proportion after the fashion of eutectic and eutectoid mixtures.

Let us now apply the teachings of the phase rule to the iron-carbon equilibrium diagram (Fig. 437). The number and kinds of phases existing at different temperatures, and for different proportions of the components, iron and carbon, have been clearly indicated and will be readily understood in view of the foregoing considerations. Above the liquidus *LEL'* all alloys are composed of but one liquid phase, and have, therefore, two degrees of freedom; between the liquidus and solidus, that is, in the region *LSE* and *L'S'E*, two phases are present, liquid solution plus solid solution (austenite), or liquid solution plus solid Fe_3C , hence the corresponding alloys have here but one degree of freedom; alloys of composition *E* and at the corresponding temperature are evidently made up of three phases, namely liquid solution plus solid austenite plus solid cementite, being, therefore, non-variant; in the region *LADS* all alloys being composed of but one phase, namely, solid austenite, are bivariant; at *D* the alloy contains three phases, ferrite, cementite, and austenite, and is, therefore, non-variant; in the area *DSS'F* two phases are present, solid solution (austenite) plus cementite, and the system has but one degree of freedom. If, as is often the case, cementite is in this region decomposed into iron and graphite the alloys are for the time being non-variant, becoming again univariant on the complete disappearance of cementite. In the region *ABH* beta iron and austenite are present, the alloys having in consequence but one degree of freedom; in the region *BCDH* alpha ferrite and austenite are present and the alloys, therefore, are univariant. Finally below *CDF* three possible cases should be considered: (I) the cementite formed during solidification and subsequent cooling

¹ All investigators do not agree as to the homogeneity, that is the phase-like character of martensite, some still regarding it as an aggregate.

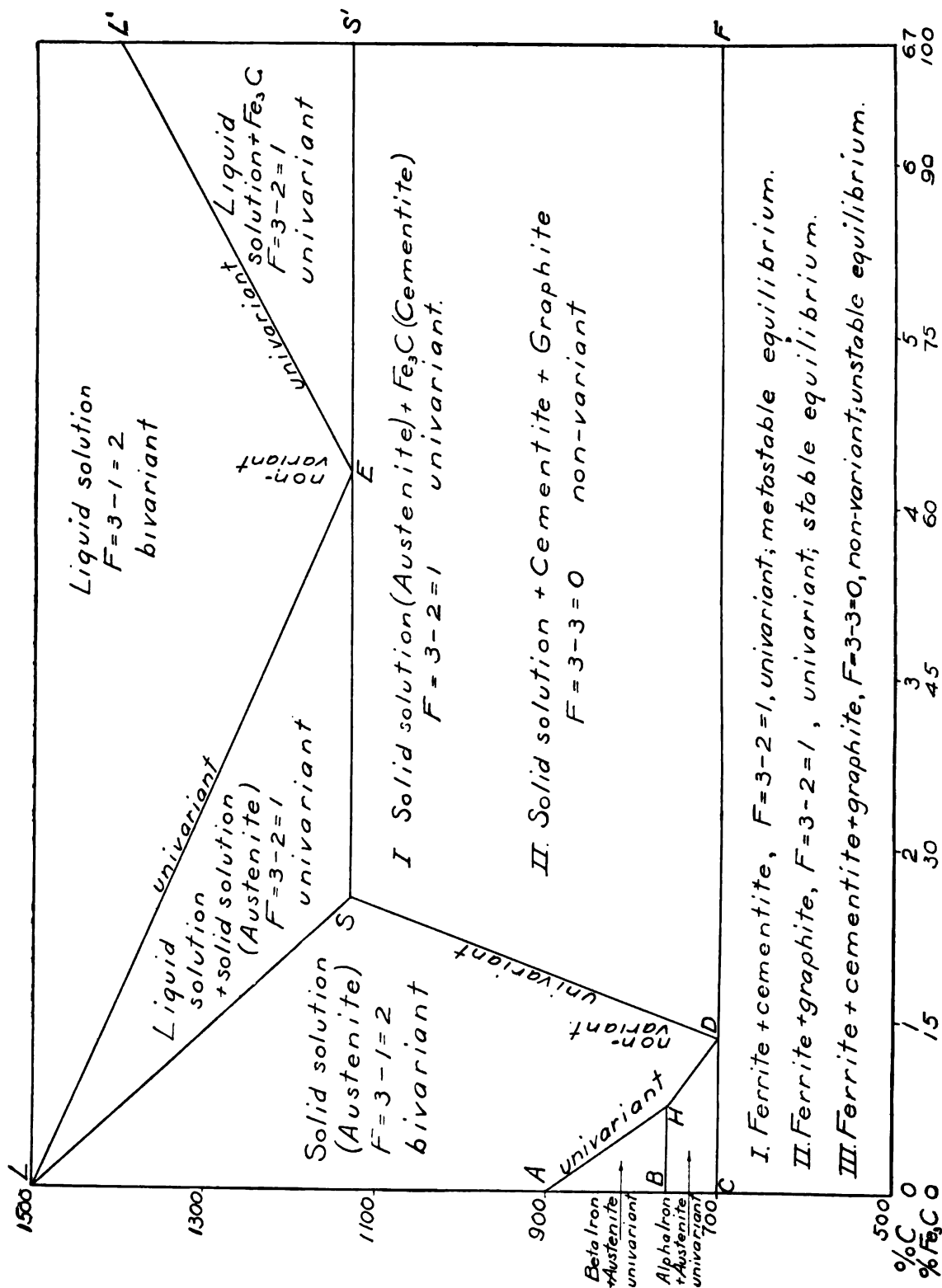


Fig. 437. - Equilibrium of iron-carbon alloys according to the Phase Rule.

remains unchanged, in which case the alloys are made up of the two phases ferrite and cementite, being, therefore, univariant, their equilibrium, however, as previously explained, is supposed to be metastable; (II) the cementite has been completely converted into ferrite and graphite, only those two phases being present, undoubtedly representing the stable equilibrium of all iron-carbon alloys; (III) the dissociation of cementite has been incomplete, both cementite and graphite being present, which with ferrite give three phases, the corresponding alloys being non-variant and, therefore, their equilibrium unstable. Condition (I) generally prevails in all grades of steel, and is readily produced in cast iron by rapid cooling especially in the absence of considerable silicon, the resulting alloys being known as white cast iron. Condition (II) never obtains in steel, but may be produced in highly carburized alloys by very slow cooling through and below solidification, especially in the presence of much silicon and in the absence of manganese and sulphur. Condition (III) is the condition of the gray cast irons of commerce, their compositions and other influences prevailing during their cooling being such as to cause the graphitizing of varying proportions of cementite.

APPENDIX

REPORT OF COMMITTEE 53 OF THE INTERNATIONAL ASSOCIATION FOR TESTING MATERIALS

ON THE NOMENCLATURE OF THE MICROSCOPIC SUBSTANCES AND STRUCTURES OF STEEL AND CAST IRON

Presented by the Chairman H. M. HOWE and the Secretary of the Committee ALBERT SAUVEUR
at the VIth Congress, New York, September, 1912

The Committee for studying this problem is constituted as follows:

Professor H. M. HOWE, Chairman, New York.

Professor ALBERT SAUVEUR, Secretary, Cambridge, Mass.

Members: F. OSMOND, Paris; Dr. H. C. H. CARPENTER, Manchester; Prof. W. CAMPBELL, New York; Prof. C. BENEDICKS, Stockholm; Prof. F. WÜST, Aachen; Prof. A. STANSFIELD, Montreal; Dr. J. E. STEAD, Middlesbrough; Prof. L. GUILLET, Paris; Prof. E. HEYN, Berlin-Lichterfelde; Dr. W. ROSENHAIN, Teddington.

I. GENERAL PLAN

We first enumerate the substances of such importance as to warrant it, indicating roughly their constitution, and then define and describe certain of them.

The conditions which we meet are (1) that we need definitions on which all can agree; and this implies that they must be free from all contentious matter and be based on what all admit to be true; (2) that the reader must needs know the current theories as to the constitution of these substances, and these theories are necessarily contentious. We meet these conditions by the plan of giving (1) the *Name* which we recommend for general use, followed immediately in parentheses by the other names used widely enough to justify recording them; (2) the *Definition* proper, based on an undisputed quality, e.g. that of austenite, which we base on its being an iron-carbon solid solution, purposely omitting all reference to the precise nature of solvent and solute; and (3) *Constitution*, etc., etc., in which we give the current theories as to the nature of solvent and solute and appropriate descriptive matter.

The distinction between these three parts should be understood. (1) The *Names* actually used are matters of record and indisputable. (2) The *Definitions* are matters of convention or treaty, binding on the contracting parties, though subject to denouncement, preferably based on some determinable property of the thing defined as distinguished from any theory as to its nature, or if necessarily based on any theory it should be a theory which is universally accepted. It is a matter purely of convention and general convenience what individual property of the thing defined shall form the basis of the definition. The name and the definition should endure permanently, except in the case of a definition based on an accepted theory, which must be

changed if the theory should later be disproved. (3) *Theories* and *Descriptions* are not matters of agreement or convention but dependent on observation, and therefore always subject to be changed by new discoveries. They are temporary in their nature as distinguished from the names and definitions which should be fixed, at least relatively.

This case of austenite illustrates the advantage of non-indicative names. The names which we propose to displace, "gamma iron" and "mixed crystals," imply definite theories as to the nature of austenite, and hence might have to be abandoned in case those theories were later disproved. The name "austenite" implies nothing, like mineralogical names in general, and hence is stable in itself. Our infant branch of science may well learn from its elder sister, which has tried and proved the advantage of this non-indicative naming.

In those cases in which a name has been used in more than one sense we advise the retention of one and the abandonment of the others, having obtained the consent of the proposers of such names for their abandonment.

Many whose judgment we respect object to our including certain of the less used names, e.g. from *i* to *n* in our list, holding them either to be confusing or to be needless.

It is true that several names (hardenite, martensite, sorbite, etc.), have been used with various meanings, and hence confusingly, in spite of which most of them should be retained, each with a single sharp-cut definition, because they are so useful.

As regards the alleged needlessness of certain names it is for each writer to decide whether he does or does not need names with nice shades of meaning, such as osmondite and troosto-sorbite. Those who look only at the general outlines and not at the details have no right to forbid the workers in detail from having and using words fitting their work; nor have those whose needs are satisfied by the three primary colors a right to forbid painters, dyers, weavers, and others from naming the many shades with which they are concerned. Like the lexicographer we must serve the reader by explaining those words which he will meet, whether we individually use or condemn them. We feel that we have exhausted our powers in cautioning writers that certain words are rare and not likely to be understood by most readers, or are improper for any reason, and in urging the complete abandonment of those withdrawn by their proposers.

Needless words will die a natural death; needed ones we cannot kill. The good we might do in hastening the death of the moribund by omitting them from this report is less than the good we do by teaching their meaning to those who will meet them in ante-mortem print. These readers have rights. We serve no class, but the whole.

Illustrations. — At the end of the several descriptions the reader is referred to good illustrations in Osmond and Stead's "Microscopic Analysis of Metals," Griffin & Co., London, 1904.

II. LIST OF MICROSCOPIC SUBSTANCES

The microscopic substances here described consist of

1. *Metals*, true phases, like the minerals of nature. These are either elements, definite chemical compounds, or solid solutions and hence consisting of definite substances in varying proportions. These include austenite, ferrite, cementite, and graphite.

2. *Aggregates*, like the petrographic entities as distinguished from the true minerals. These mixtures may be in definite proportions, i.e. eutectic, or eutectoid mixtures (ledeburite, pearlite, steadite), or in indefinite proportions (troostite, sorbite). Those aggregates which are important for any reason are here described.

(Many true minerals, such as mica, felspar, and hornblende, are divisible into several different species so that these true mineral names may be either generic or specific. These genera and species are definite chemical compounds in which one element may replace another. Other minerals, such as obsidian, are solid solutions in varying proportions, and in these also one element may replace another. Metarals like minerals differ from aggregates in being severally chemically homogeneous.)

These two classes may be cross classified into:

- (A) The iron-carbon series, which come into being in cooling and heating.
- (B) The important impurities, manganese sulphide, ferrous sulphide, slag, etc.
- (C) Other substances.

The most prominent members of the iron-carbon series are:

- I. molten iron, metaral, molten solution, but hardly a microscopic constituent;
- II. the components which form in its solidification:

- (a) austenite, solid solution of carbon or iron carbide in iron, metaral,
- (b) cementite, definite metaral, Fe_3C ,
- (c) graphite, definite metaral, C;

III. the transition substances which form through the transformation of austenite during cooling:

- (d) martensite, metaral of variable constitution; its nature is in dispute;
- (e) troostite, indefinite aggregate, uncoagulated mixture,
- (f) sorbite, indefinite aggregate, chiefly uncoagulated pearlite plus ferrite or cementite;

IV. products¹ of the transformation of austenite:

- (g) ferrite,
- (h) pearlite.

This transformation may also yield cementite and graphite as end products in addition to those under *b* and *c*.

In addition to the above, the names of which are universally recognized and in general use, the following names have been used more or less:

- (i) ledeburite (Wüst), definite aggregate, the austenite-cementite eutectic;
- (j) ferronite (Benedicks), hypothetical definite metaral, β iron containing about 0.27 per cent of carbon;
- (k) steadite (Sauveur), definite aggregate, the iron-phosphorus eutectic (rare); and three transition stages in the transformation of austenite, viz.:
- (l) hardenite (Arnold), collective name for the austenite and martensite of eutectoid composition;
- (m) osmondite (Heyn), boundary stage between troostite and sorbite;
- (n) troosto-sorbite (Kourbatoff), indefinite aggregate, the troostite and the sorbite which lie near the boundary which separates these two aggregates (obsolescent).

¹In hypo-eutectoid steels these habitually play the part of end products, though according to the belief of most the true end of the transformation is not reached till the whole has changed into a conglomerate of ferrite plus graphite.

III. DEFINITIONS AND DESCRIPTIONS

Carbon-Iron Equilibrium Diagram, Figure 438.— Under the several substances about to be described an indication will be given of the parts of the carbon-iron equilibrium diagram Figure 438 to which they severally correspond.

Austenite, Osmond (Fr. Austénite, Ger. Austenit, called also mixed crystals and gamma iron. Up to the year 1900 often called martensite and wrongly sometimes still so called). Metaral of variable composition.

Definition.— The iron-carbon solid solution as it exists above the transformation

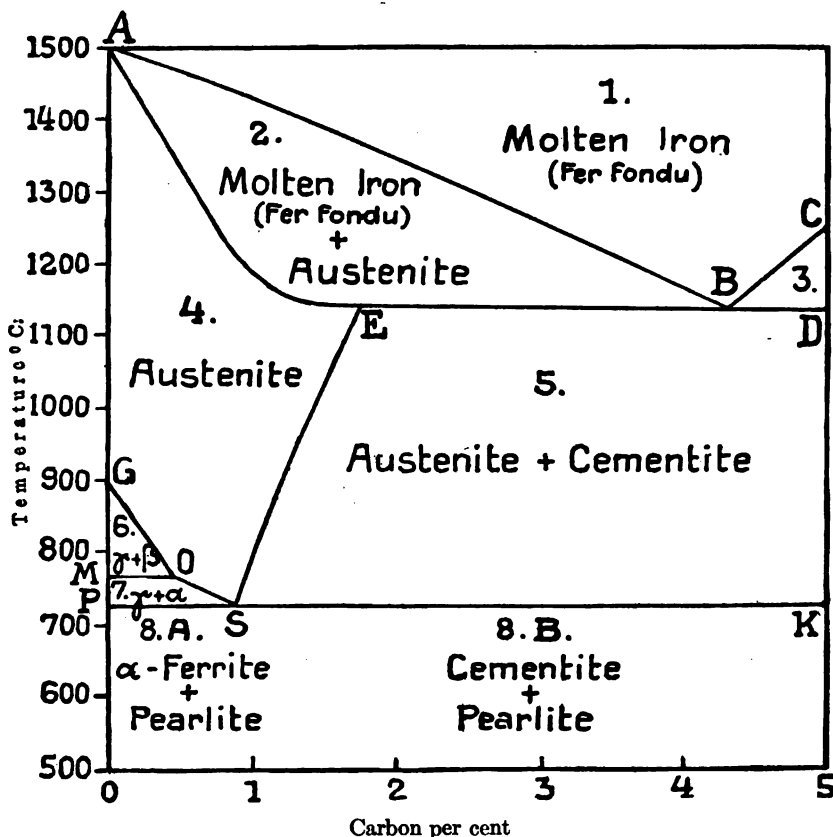


Fig. 438. — A_1 : The line PSK is often called " A_1 ". A_3 : The line GOS is often called " A_3 ", and this name is sometimes applied to the line SE.

range or as preserved with but moderate transformation at lower temperatures, e.g. by rapid cooling, or by the presence of retarding elements (Mn, Ni, etc.), as in 12 per cent manganese steel and 25 per cent nickel steel.

Constitution and Composition.— A solid solution of carbon or iron carbide (probably Fe_3C) and gamma iron, normally stable only above the line PSK of the carbon-iron diagram. It may have any carbon content up to saturation as shown by the line SE, viz.: about 0.90 per cent at S (about 725 deg. C.) to 1.7 per cent at E (about 1130 deg.). The theory that the iron and the carbide or carbon, instead of being dissolved in each other, are dissolved in a third substance, the solution of eutectoid com-

position (Fe_2C , called hardenite) is not in accord with the generally accepted theory of the constitution of solutions, and is not entertained widely or by any member of this committee.

Crystallization. — Isometric. The idiomorphic vug crystals are octahedra much elongated by parallel growth. The etched sections show much twinning. (Osmond and most authorities.) Le Chatelier believes it to be rhombohedral. Cleavage octahedral.

Varieties and Genesis. — (1) Primary austenite formed in the solidification of carbon steel and hypo-eutectic cast iron; (2) eutectic austenite, interstratified with eutectic cementite, making up the eutectic formed at the end of the solidification of steel containing more than about 1.7 per cent of carbon, and of all cast iron.

Equilibrium. — It is normal and in equilibrium in Region 4, and also associated with beta iron in Region 6, with α iron in Region 7, and with cementite in Region 5. It should normally transform into pearlite with either ferrite or cementite on cooling past A_1 into Region 8.

Transformation. — In cooling slowly through the transformation range, $A_3 - A_1$, austenite shifts its carbon content spontaneously through generating pro-eutectoid ferrite or cementite, to the eutectoid ratio, about 0.90 per cent, and then transforms with increase of volume at A_1 into pearlite, q.v., with which the ejected ferrite or cementite remains mixed. Rapid cooling and the presence of carbon, manganese, and nickel obstruct this transformation, (1) retarding it, and (2) lowering the temperature at which it actually occurs, and in addition (3) manganese and nickel lower the temperature at which in equilibrium it is *due*. Hence, by combining these four obstructing agents in proper proportions the transformation may be arrested at any of the intermediate stages, martensite, troostite, or sorbite,¹ q.v., and if arrested in an earlier stage it can be brought to any later desired stage by a regulated reheating or "tempering." For instance, though a very rapid cooling in the absence of the three obstructing elements checks the transformation but little and only temporarily, yet if aided by the presence of a little carbon it arrests the transformation wholly in the martensite stage; and in the presence of about 1.50 per cent of carbon such cooling retains about half the austenite so little altered that it is "considerably" softer than the usually darker needles of the surrounding martensite, with which it contrasts sharply. Again, either (a) about 12 per cent of manganese plus 1 per cent of carbon, or (b) 25 per cent of nickel, lower and obstruct the transformation to such a degree that austenite persists in the cold apparently unaltered, even through a slow cooling. (Hadfield's manganese steel and 25 per cent nickel steel, manganiferous and nickeliferous austenite respectively.)

Occurrence. — When alone (12 per cent manganese and 25 per cent nickel steel and Maurer's 2 per cent carbon plus 2 per cent manganese austenite) polyhedra, often coarse, much twinned at least in the presence of martensite, and readily developing slip bands. In hardened high-carbon steel it forms a ground mass pierced by zigzag needles and lances of martensite.

Etching. — All the common reagents darken it much more than cementite, less

¹ Though the transformation can be arrested in such a way as to leave the whole of the steel in the condition of martensite, it is doubted by some whether it can be so arrested as to leave the whole of it in any of the other transition stages. Troostite and sorbite caused by such arrest are habitually mixed, troostite with martensite or sorbite or both, and sorbite with pearlite or troostite or both.

than troostite or sorbite, and usually less, though sometimes more, than martensite, which is recognized by its zigzag shape and needle structure. With ferrite and pearlite it is never associated.

Physical Properties. — Maurer's austenite of 2 per cent manganese plus 2 per cent carbon is but little harder than soft iron, and 25 per cent nickel steel and Hadfield's manganese steel are but moderately hard. Yet as usually preserved in hardened high carbon steel, the hardness of austenite does not fall very far short of that of the accompanying martensite, probably because partly transformed in cooling. (Osmond's words are that it is "considerably" softer than that martensite.)

Specific Magnetism. — Very slight unless perhaps in intense fields. In Hadfield's manganese steel and 25 per cent nickel steel, very ductile.

Illustrations. — "Microscopic Analysis of Metals," Figures 20, 50, and 51 on pp. 39, 100, and 101.

Cementite (Sorby, "intensely hard compound"; Ger. Cementit, Fr. Cémentite; Arnold, crystallized normal carbide). Definite metalal.

Definition. — Tri-ferrous carbide, Fe_3C . The name is extended by some writers so as to include tri-carbides in which part of the iron is replaced by manganese or other elements. Such carbides may be called "manganiferous cementite," etc.

Occurrence. — (a) Pearlitic as a component of pearlite, q.v.; (b) eutectic; (c) primary or pro-eutectic; (d) pro-eutectoid; (e) that liberated by the splitting up of the eutectic or of pearlite; and (f) uncoagulated in sorbite, troostite, and perhaps martensite. (c), (d), and (e) are grouped together as "free" or "massive."

Primary cementite is generated in cooling through Region 3; eutectic cementite on cooling past the line EBD; pro-eutectoid cementite in cooling through Region 5; pearlitic cementite on cooling past the line PSK, or A_1 . Though the several varieties of cementite are generally held to be all metastable, tending to break up into graphite plus either austenite above A_1 or ferrite below A_1 , yet they have a considerable and often great degree of persistence. The graphitizing tendency is completely checked in the cold but increases with the temperature and with the proportion of carbon and of silicon present, and is opposed by the presence of manganese.

Crystallization. — Orthorhombic, in plates.

Structure. — (a) Pearlitic, in parallel unintersecting plates alternating with plates of ferrite; (b) eutectic, plates forming a network filled with a fine conglomerate of pearlite with or without pro-eutectoid cementite; (c) primary, in manganiferous white cast iron, etc., in rhombohedral plates; (d) in hyper-eutectoid steel, pro-eutectoid cementite forms primarily a network enclosing meshes of pearlite through which cementite plates or spines sometimes shoot if the network is coarse; (e) cementite liberated from pearlite merges with any neighboring cementite; (f) the structure of uncoagulated cementite cannot be made out. On long heating the pro-eutectoid and pearlitic cementite spheroidize slowly, and neighboring particles merge; (g) in white irons rich in phosphorus in flat plates embedded in iron-carbon-phosphorus eutectic.

Etching, etc. — After polishing stands in relief. Brilliant white after etching with dilute hydrochloric or picric acid; darkened by boiling with solution of sodium picrate in excess of sodium hydrate.

Physical Properties. — Hardest component of steel. Hardness = 6 of Mohs scale. Scratches glass and felspar but not quartz; very brittle. Specific magnetism about two thirds that of pure iron.

Illustrations. — “Microscopic Analysis of Metals,” Figures 42 and 43 on pp. 84, 85.

Martensite (Fr. Martensite, Ger. Martensit). Metaral. Its nature is in dispute.

Definition. — The early stage in the transformation of austenite characterized by needle structure and great hardness, as in hardened high-carbon steel.

Constitution. — I. (Osmond and others.) A solid solution like austenite, q.v., except that the iron is partly beta, whence its hardness, and partly alpha, whence its magnetism in mild fields. II. (Le Chatelier.) The same except that its iron is essentially alpha, and the hardness due to the state of solid solution. III. (Arnold.) A special structural condition of his “hardenite” (austenite); not widely held. IV. A solid solution in gamma iron. V. (Benedicks.) The same as I, except that the iron is wholly beta and that beta iron consists of alpha iron containing a definite quantity of gamma iron in solution.

Equilibrium. — It is not in equilibrium in any part of the diagram, but represents a metastable condition in which the metal is caught during rapid cooling, in transit between the austenite condition stable above the line A_1 and the condition of ferrite plus cementite into which the steel habitually passes on cooling slowly past the line A_1 .

Occurrence. — The chief constituent of hardened carbon tool steels, and of medium nickel and manganese steels. In still less fully transformed steels (1.50 per cent carbon steel rapidly quenched, etc.) it is associated with austenite; in more fully transformed ones (lower carbon steels hardened, high carbon steels oil hardened, or water hardened and slightly tempered, or hardened thick pieces even of high carbon steel) it is associated with troostite, and with some pro-eutectoid ferrite or cementite, q.v., in hypo- and hyper-eutectoid steels respectively. In tempering it first changes into troostite; at 350 deg. – 400 deg. it passes through the stage of osmondite; at higher temperatures it changes into sorbite; and at 700 deg. into granular pearlite. On heating into the transformation range this changes into austenite, which on cooling again yields lamellar pearlite.

Characteristic specimens are had by quenching bars 1 cm. square of eutectoid steel, i.e. steel containing about 0.9 per cent of carbon, in cold water from 800 deg. C. (1472 deg. F.).

Structure. — When alone, habitually in flat plates made up of intersecting needles parallel to the sides of a triangle. When mixed with austenite, zigzag needles, lances, and shafts.

If produced by quenching after heating to 735 deg. C., it consists of minute crystallites resembling the globulites of Vogelsang, which are rarely arranged in triangular order. At times so fine as to suggest being amorphous.

Etching. — With picric acid, iodine or very dilute nitric acid etches usually darker than austenite, but sometimes lighter, always darker than ferrite and cementite, but always lighter than troostite.

Illustrations. — “Microscopic Analysis of Metals,” Figure 19 on p. 38, Figure 52 on p. 102.

Ferrite (Fr. Ferrite, Ger. Ferrit). Definite metaral.

Definition. — Free alpha iron.

Composition. — Nearly pure iron. It may contain a little phosphorus and silicon but its carbon content, if any, is always small, at the most not more than 0.05 per cent, and perhaps never as much as 0.02 per cent.

Occurrence. — (a) *Pearlitic* as a component of pearlite, q.v.; (b) pro-eutectoid ferrite generated in slow cooling through the transformation range; (c) that segregated from pearlite, i.e. set free by the splitting up of pearlite, especially in low carbon steel; (d) *uncoagulated* as in sorbite, and probably troostite. (b) and (c) are classed together as free or massive.

Thus ferrite is normal and stable in regions 7 and 8.

Crystallization. — Isometric, in cubes or octahedra.

Structure. — (a) Pearlitic ferrite, unintersecting parallel plates alternating with plates of cementite; (b) pro-eutectoid ferrite in low carbon steel forms irregular polygons, each with uniform internal orientation. In higher carbon steel after moderately slow cooling, especially in the presence of manganese, it forms a network enclosing meshes of pearlite. In slower cooling this network is replaced by irregular grains separated by pearlite; (c) the ferrite set free by the splitting up of pearlite merges with the pro-eutectoid ferrite, if any; (d) the structure of the ferrite in sorbite, etc., cannot be made out.

Etching. — Dilute alcoholic nitric or picric acid on light etching leaves the ferrite grains white with junctions which look dark. Deeper etching, by Heyn's reagent or its equivalent, reveals the different orientation of the crystals or grains, (a) as square figures parallel to the direction of the etched surface, (b) as plates which dip at varying angles and become dark or bright when the specimen is rotated under oblique illumination. Still deeper etching reveals the component cubes (etching figures, Ätzfiguren), at least if the surface is nearly parallel to the cube faces.

Physical Properties. — Soft; relatively weak (tenacity about 40,000 lbs., per sq. in.); very ductile; strongly ferro-magnetic; coercitive force very small.

Grain Size. — For important purposes (1) etch deeply enough, e.g. with copper-ammonium chloride, to reveal clearly the junctions of the grains; (2) count on a photograph of small magnification the number of grains in a measured field so drawn as to exclude fragments of grains; after (3) determining the true grain boundaries by examination under high powers (Heyn's method). Deep nitric acid etching is inaccurate, because an apparent grain boundary may contain several grains.

Illustrations. — "Microscopic Analysis of Metals," Figures 41, 56 on pp. 79, 116.

Osmondite (Fr. Osmondite, Ger. Osmondit).

Definition. — That stage in the transformation of austenite at which the solubility in dilute sulphuric acid reaches its maximum rapidity. Arbitrarily taken as the boundary between troostite and sorbite.

Earlier Definition. — Defined by the Vth Congress as having the "maximum solubility in acids and by a maximum coloration under the action of acid metallographic reagents." The present definition is confined to maximum rapidity of dissolving, because we do not yet know that this in all cases co-exists with the maximum depth of coloration, and in any case in which these two should not co-exist, the old definition does not decide which is true osmondite.

Constitution. — The following hypotheses have been suggested, none of which has firm experimental foundation: (1) A solid solution of carbon or an iron carbide in alpha iron. (2) The colloidal system of Benedicks in its purity, troostite being this system while forming at the expense of martensite, and sorbite, being this system coagulating and passing into pearlite. (3) The stage of maximum purity of amorphous alpha iron on the way to crystallizing into ferrite.

Occurrence. — Hardened carbon steel of about 1 per cent of carbon when reheated

(tempered) to 350–400 deg. C. passes through the stage of troostite to that of osmondite, and on higher heating to that of sorbite. What variation if any from this temperature is needed to bring hardened steel of other carbon content to the osmondite stage is not known. In that it represents a true boundary state between troostite and sorbite it differs in meaning from troosto-sorbite, which embraces both the troostite and the sorbite which lie near this boundary. Indeed osmondite has sometimes been used in this looser sense. Writers are cautioned that, however useful these terms may prove for making these nice discriminations, they are not likely to be familiar to general readers.

Etching. — According to Heyn it differs from troostite and sorbite in being that stage in tempering which colors darkest on etching with alcoholic hydrochloric acid.

The present definition and description of osmondite should displace previous ones, because they have the express approval of Professor Heyn, the proposer of the name, and M. Osmond himself.

Ferronite (Fr. Ferronite, Ger. Ferronit) (Benedicks). Hypothetical definite metal.

Definition. — Solid solution of about 0.27 per cent of carbon in beta iron.

Occurrence (hypothetical). — In slowly cooled steels and cast iron containing 0.50 per cent of combined carbon or more, that which is generally believed to be ferrite, whether pearlitic or free, is supposed by Benedicks to be ferronite.

Hardenite (Fr. Hardenite, Ger. Hardenit).

Definition. — Collective name for austenite and martensite of eutectoid composition. It includes such steel (1) when above the transformation range, and (2) when hardened by rapid cooling.

Observations. — On the generally accepted theory that austenite is a solid solution of carbon or an iron carbide in iron, hardenite is the solution of the lowest transformation temperature, i.e. the eutectoid. The theory that instead it is a definite chemical compound, Fe_2C , is considered under Austenite. Its proposer includes under hardenite both eutectoid (0.90 per cent carbon) austenite when above the transformation range and the martensite into which that austenite shifts in rapid cooling (hardening).

Other Meanings. — Originally (Howe, 1888) collective name for austenite and martensite of any composition in carbon steel. Osmond (1897), austenite saturated with carbon. Both these meanings are withdrawn by their proposers.

Pearlite (Sorby's "pearly constituent." At first written "pearlyte" Fr. Perlite, Ger. Perlit). Aggregate.

Definition. — The iron-carbon eutectoid, consisting of alternate masses of ferrite and cementite.

Constitution and Composition. — A conglomerate of about 6 parts of ferrite to 1 of cementite. When pure, contains about 0.90 per cent of carbon, 99.10 per cent of iron.

Occurrence. — Results from the completion of the transformation of austenite brought spontaneously to the eutectoid carbon content, and hence occurs in all carbon steels and cast iron containing combined carbon and cooled slowly through the transformation range, or held at temperatures in or but slightly below that range, long enough to enable the ferrite and cementite to coagulate into a mass microscopically resolvable. Hence it is the normal constituent in Region 8. Its ferrite is stable but its cementite is metastable and tends to transform into ferrite and graphite.

Varieties and Structure. — Because pearlite is formed by the coagulation of the

ferrite and cementite initially formed as the irresoluble emulsion, sorbite, (Arnold's sorbitic pearlite) there are the indefinitely bounded stages of *sorbitic pearlite* (Arnold's normal pearlite), i.e. barely resolvable pearlite, in the border-land between sorbite and laminated pearlite; *granular pearlite*, in which the cementite forms fine globules in a matrix of ferrite; and *laminated* or *lamellar pearlite*, consisting of fine, clearly defined, non-intersecting, parallel lamellæ alternately of ferrite and cementite. The name *granular pearlite* was first used by Sauveur to represent what is now called sorbite. This meaning has been withdrawn.

An objection to Arnold's name "normal pearlite" is that it is likely to mislead. "Normal" here apparently refers to arising under normal conditions of cooling, but (1) it rather suggests structure normal for pearlite, which surely is the lamination characteristic of eutectics in general, and (2) the general reader has no clue as to what conditions of cooling are here called normal. Many readers are not manufacturers, and even in manufacture itself air cooling is normal for one branch and extremely slow furnace cooling for another. Arnold calls troostite "troostitic pearlite" and sorbite "sorbitic pearlite." This is contrary to general usage, which restricts pearlite to microscopically resolvable masses.

Etching. — After etching with dilute alcoholic nitric or picric acid it is darker than ferrite or cementite but lighter than sorbite and troostite. A magnification of at least 250 diameters is usually needed for resolving it into its lamellæ, though the pearlite of blister steel can often be resolved with a magnification of 25 diameters. The more rapidly pearlite is formed, the higher the magnification needed for resolving it.

Illustrations. — Lamellar pearlite. Osmond and Stead, "Microscopic Analysis," Figure 11 on p. 19, Granular pearlite, *idem*, Figure 18 on p. 36; Heyn and Bauer, "Stahl und Eisen," 1906, Figure 14, opposite p. 785.

Graphite (Ger. Graphit, Fr. Graphite). Definite metal.

Definition. — The free elemental carbon which occurs in iron and steel.

Composition. — Probably pure carbon, identical with native graphite.

Genesis. — Derived in large part, and according to Goerens wholly, from the decomposition of solid cementite. Others hold that its formation as kish may be from solution in the molten metal, and that part of the formation of temper graphite may be from elemental carbon dissolved in austenite. It is the stable form of carbon in all parts of the diagram.

Occurrence. — (1) as kish, flakes which rise to the surface of molten cast iron and usually escape thence;

(2) as thin plates, usually curved, e.g. in gray cast iron, representing carbon which has separated during great mobility, i.e. near the melting range;

(3) as temper graphite (Ger. Temperkohle, Ledebur) pulverulent carbon which separates from cementite and austenite, especially in the annealing process for making malleablized castings.

Graphite and ferrite are sometimes associated in a way which suggests strongly that they represent a graphite-austenite eutectic. But the existence of such a true eutectic is doubted by most writers.

Properties. — Hexagonal. H. 1–2. Gr. 2.255. Streak black and shining, luster metallic; macroscopic color, iron black to dark steel gray, but always black when seen in polished sections of iron or steel under the microscope; opaque; sectile; soils paper; flexible; feel, greasy.

Troostite (Fr. Troostite, Ger. Troostit). Probably aggregate. (Arnold, troostitic pearlite.)

Definition. — In the transformation of austenite, the stage following martensite and preceding sorbite (and osmondite if this stage is recognized).

Constitution and Composition. — An uncoagulated conglomerate of the transition stages. The degree of completeness of the transformation represented by it is not definitely known and probably varies widely. Osmond and most others believe that the transformation, while generally far advanced, yet falls materially short of completion; but Benedicks and Arnold (9) believe that it is complete. The former belief that it is a definite phase, e.g. a solid solution of carbon or an iron carbide in either β or γ iron, is abandoned. Its carbon content like that of austenite and martensite varies widely.

Occurrence. — It arises either on reheating hardened (e.g. martensitic steel) to slightly below 400 deg., or on cooling through the transformation range at an intermediate rate, e.g. in small pieces of steel when quenched in oil, or quenched in water from the middle of the transformation range, or in the middle of larger pieces quenched in water from above the transformation range. With slightly farther reheating it changes into sorbite; with higher heating into sorbitic pearlite, then slowly into granular pearlite, and probably indirectly into lamellar pearlite. It occurs in irregular, fine-granular or almost amorphous areas, colored darker by the common etching reagents than the martensite or sorbite accompanying it. A further common means of distinguishing it from sorbite is that it is habitually associated with martensite, whereas sorbite is habitually associated with pearlite.

Areas near the boundary between troostite and sorbite are sometimes called troosto-sorbite.

Properties. — Hardness, intermediate between that of the martensitic and the pearlitic state corresponding to the carbon content of the specimen. In general the hardness increases, the elastic limit rises, and the ductility decreases, as the carbon content increases. Its ductility is increased rapidly and its hardness and elastic limit lowered rapidly by further tempering, which affects it much more markedly than sorbite.

Sorbite (Fr. Sorbite, Ger. Sorbit). Aggregate. (Arnold, sorbitic pearlite.)

Definition. — In the transformation of austenite, the stage following troostite and osmondite if the stage is recognized, and preceding pearlite.

Constitution and Composition. — Most writers believe that it is essentially an uncoagulated conglomerate of irresoluble pearlite with ferrite in hypo- and cementite in hyper-eutectoid steels respectively, but that it often contains some incompletely transformed matter.

Occurrence. — The transformation can be brought to the sorbitic stage (1) by reheating hardened steel to a little above 400 deg., but not to 700 deg. at which temperature it coagulates into granular pearlite; (2) by quenching small pieces of steel in oil or molten lead or even by air cooling them; (3) by quenching in water from just above the bottom of the transformation range, A_{r1} . Sorbite is ill-defined, almost amorphous, and is colored lighter than troostite but darker than pearlite by the usual etching reagents. It differs further from troostite in being softer for given carbon content, and usually in being associated with pearlite instead of martensite, and from pearlite in being irresoluble into separate particles of ferrite and cementite.

As sorbite is essentially a mode of aggregation it cannot properly be represented

on the equilibrium diagram. Its components at all times tend to coagulate into pearlite, yet it remains in its uncoagulated state at all temperatures below 400 deg.

Properties. — Though slightly less ductile than pearlitic steel for given carbon content, its tenacity and elastic limit are so high that a higher combination of these three properties can be had in sorbitic than in pearlitic steels by selecting a carbon content slightly lower than would be used for a pearlitic steel. Hence the use of sorbitic steels, e.g. first hardened and then annealed cautiously, for structural purposes needing the best quality.

Manganese Sulphide (Fr. Sulphur de Manganèse, Ger. Schwefelmangan), MnS (Arnold and Waterhouse). Metaral.

Occurrence, etc. — Sulphur combines with the manganese present in preference to the iron, forming pale dove or slate gray masses, rounded in castings, elongated in forgings.

Ferrous Sulphide (Fr. Sulphure de Fer, Ger. Schwefeleisen), FeS . Metaral.

Occurrence. — The sulphur not taken up by the manganese forms ferrous sulphide, FeS , which, probably associated in part with iron as an Fe-FeS eutectic, forms by preference more or less continuous membranes surrounding the grains of pearlite. Color, yellow or pale brown.

Sulphur Prints. — When silk impregnated with mercuric chloride and hydrochloric acid (Heyn's and Bauer's method) or bromide paper moistened with sulphuric acid (Baumann's method) is pressed on polished steel, the position of the sulphur-bearing areas, whether of FeS or MnS , records itself by the local blackening which the evolved H_2S causes. Phosphorus bearing areas also blacken Baumann's bromide paper.

MISCELLANEOUS

Eutectoid, Saturated, etc. — The iron-carbon eutectoid is pearlite. Steel with more carbon than pearlite is called hyper-eutectoid, that with less is called hypo-eutectoid. Arnold's names "saturated," "unsaturated," and "supersaturated," for eutectoid, hypo-eutectoid, and hyper-eutectoid steel respectively, have considerable industrial use in English-speaking countries, but are avoided by most scientific writers on the ground that they are misleading, because, e.g. there is only one specific temperature, A_1 , at which eutectoid steel is actually saturated, and, if any other temperature is in mind, that steel is not saturated. Above A_1 it is clearly undersaturated.

The objection to the names sorbite, troostite, martensite, and austenite, that each of them covers steel of a wide range of carbon content, is to be dismissed because a like objection applies with equal force to every generic name in existence.

The theoretical matter in this report is given solely for exposition and the committee disclaims the intent to impose any theory. This report is offered for adoption subject to this disclaimer on the ground that the adoption of theories is beyond the powers of a Congress.

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